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TRW, Inc.
Redondo Beach

Prepared for

Industrial Environmental Research Lab.
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SOURCE TEST AND EVALUATION REPORT:
D.H. MITCHELL UNIT NO. 11, NORTHERN INDIANA PUBLIC SERVICE CO.

April 1981

by:

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EPA Contract No. 68-02-2197
Project Officer: Michael C. Osborne

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16. ABSTRACT

The report gives results of a comprehensive multimedia emissions assessment on NIPSCo's Dean H. Mitchell unit 11 boiler, equipped with an ESP for particulate control and a Wellman-Lord/Allied Chemical flue gas desulfurization (FGD) system. Levels 1 and 2 procedures were used to characterize pollutant emissions in gaseous, liquid, and solid waste streams. Flue gas analyses indicated SO_2 emissions of 266 ng/J after 89% removal by FGD. Primary sulfate emissions of 20.8 ng/J comprised 5 mole % of the total sulfur species emitted. Average emissions of NO_x (as NO_2) were 265 ng/J at the 70% boiler load maintained during the test. CO emissions were estimated to be 16 ng/J, on the average, based on measurements at the air heater inlet. Particulate emissions (exclusive of H_2SO_4 aerosol) were 2.6 ng/J: 98% of the particles were smaller than 3 micrometers in diameter. H_2SO_4 aerosol emissions were 3.7-10.4 ng/J, or more, and were generally smaller than 0.5 micrometer in diameter. Total organic emissions were 0.5-1.3 ng/J, consisting primarily of C1-C6 compounds. POMs were not detected at either the scrubber inlet or outlet. Concentrations of elements in flue gas after scrubbing were below DMEGs and AMEGs in all cases. Elemental concentrations in clarifier overflow, the only liquid waste discharged from the site, did not exceed health DMEGs.

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Assessments	Aerosols	Stationary Sources	14B	
Flue Gases	Dust	Environmental Assessment	21B	11G
Boilers	Carbon Monoxide		13A	
Coal	Organic Compounds	Particulate	21D	07C
Sulfur Oxides	Fly Ash		07B	
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ABSTRACT

A comprehensive multimedia emissions assessment was performed on NIPSCO's Dean H. Mitchell No. 11 boiler. This unit is equipped with an ESP for particulate control and a Wellman-Lord/Allied Chemical flue gas desulfurization (FGD) system. Level 1 and Level 2 procedures were used to characterize pollutant emissions in gaseous, liquid, and solid waste streams.

Flue gas analyses indicated SO_2 emissions of 266 ng/J after 89% removal by the FGD. Primary sulfate emissions of 20.8 ng/J comprised 5 mole percent of the total sulfur species emitted. Average emissions of NO_x (as NO_2) were 265 ng/J at the 70 percent boiler load maintained during the test period. Carbon monoxide emissions were estimated to be 16 ng/J, on the average, based on measurements at the air heater inlet. Particulate emissions (exclusive of H_2SO_4 aerosol) were 2.6 ng/J and 98 percent of the particles were smaller than 3 μm in diameter. H_2SO_4 aerosol emissions were 3.7-10.4 ng/J, or more, and were generally smaller than 0.5 μm in diameter. Total organic emissions ranged from 0.5 to 1.3 ng/J and consisted primarily of C_1-C_6 compounds. POMs were not detected at either the scrubber inlet or outlet. Concentrations of elements in the flue gas after scrubbing were below DMEGs and AMEGs in all cases. Emissions of NO_3^-, Cl^-, and F^- were 0.004, 0.25-0.34, and 0.033 ng/J, respectively. Emission concentrations of Cl^- and F^- were below their respective DMEGs. Flue gas pollutant concentrations were also determined at the air heater inlet and scrubber inlet.

Elemental concentrations in clarifier overflow, the only liquid waste discharged from the site, did not exceed health DMEGs although concentrations of Al, Ca, Cd, Fe, Ni, P, and Pb exceeded ecology DMEGs. However, Ca, Cd, Ni and Pb are present in the process feedwater from Lake Michigan at concentrations similar to those measured in the clarifier overflow. Total organic concentrations in the liquid waste were 0.108-0.117 g/m^3 and consisted primarily of high molecular weight compounds ($>C_{16}$). Organic concentrations in the process feedwater from Lake Michigan were 0.235-0.242 g/m^3. No POMs were detected in the liquid waste. Individual liquid waste streams including

the prescrubber slurry liquids, thiosulfate purge and melt tank purge were also evaluated.

Fly ash, prescrubber solids, and ash pond sludge contained several elements at concentrations exceeding DMEGs. Elements of principal concern included Al, As, Fe, Ni, and P. Organic concentrations were approximately 4.7 mg/kg and consisted primarily of high molecular weight compounds ($>C_{16}$). POMs were not detected in the solid waste. Sodium salts in the thiosulfate and melt tank purge streams, soda ash, and product sulfur were also analyzed.

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1. INTRODUCTION

This report details the results of a comprehensive multimedia emissions assessment performed on the Northern Indiana Public Service Company's (NIPSCO) Dean H. Mitchell No. 11 utility boiler in Gary, Indiana. This unit is a wall-fired, dry bottom boiler with a net electric generating capacity of 115 MW. High volatile bituminous coal from the Captain Mines No. 6 seam is normally fired in this boiler. The unit is equipped with an ESP to control particulate emissions and a Wellman-Lord (W-L) scrubber to control SO_2 emissions. Based on 1978 data, the average installed capacity for pulverized bituminous coal-fired dry bottom units is 200 MW, approximately 1.7 times larger than the test unit. Sixty percent of the installed units (79% on a capacity basis) employ ESPs for particulate control. However, the scrubber/sulfur recovery system represents the first application of Davy McKee's W-L process to a coal-fired boiler and the first combination of the W-L process with Allied Chemical's SO_2 reduction process.

2. SUMMARY AND CONCLUSIONS

A comprehensive multimedia emissions assessment was performed on the Northern Indiana Public Service Company's Dean H. Mitchell No. 11 boiler. This unit is a wall-fired, dry bottom radiant boiler with a maximum steaming capacity of 103 kg/s and a corresponding turbo-generator output of 115 MW. Normal output ranges from 46 MW to 115 MW with an average load factor of 80% or 92 MW. The unit is fueled with a high volatile bituminous coal from the Captain Mines No. 6 seam. Typical fuel ash and sulfur contents are 9.5% and 3.2%, respectively. Average ash and sulfur contents during the test period were 12.5% and 3.5% (dry bases), respectively. Particulate emissions are controlled with a cold end, American Standard Co. electrostatic precipitator (ESP) and sulfur dioxide emissions are controlled with a Wellman-Lord/Allied Chemical flue gas desulfurization (FGD) unit.

The principal waste streams from this system are bottom and fly ash, prescrubber slurry from a venturi contactor, and flue gas. Bottom ash samples from the No. 11 boiler could not be obtained because the sluice system combines ash from all units at the Mitchell station. Solid and liquid wastes are discharged to a system of three primary ash storage ponds totaling 122,000 m^3 in capacity. Solid wastes are dewatered and hauled to off-site disposal areas. Supernatant liquids are processed through either of two 14,000 m^3 clarifying ponds and discharged into Lake Michigan.

Two additional streams were being discharged from the FGD system during the test period: 1) the melt tank liquor and 2) the thiosulfate purge. These streams would be dried to produce a solid by-product during normal operation; however, equipment problems necessitated the discharge of these streams into the ash pond during the entire test period.

Average measured flue gas emissions are summarized in Table 1. Emissions data indicated an SO_2 scrubbing efficiency of 89% based upon scrubber inlet and outlet data. Sulfur dioxide levels measured at the air heater inlet appeared to be erroneously low based upon feed coal sulfur concentrations; this can be partially attributed to instrument drift, although the cause is not

TABLE 1. AVERAGE MEASURED FLUE GAS EMISSIONS

Pollutant	Emission Factor, ng/J		
	Air Heater Inlet	Scrubber Inlet	Scrubber Outlet
SO_2^{*}	$1968 \pm 145^{***}$	$2482 \pm 158^{***}$	$266 \pm 39^{***}$
Primary $SO_4^{=\dagger}$	$24.8 \pm 3.0^{***}$	$21.7 \pm 5.6^{***}$	$20.8 \pm 2.9^{***}$
$NO_x^{\ddagger}$ (as NO_2 at 70% load)	$224 \pm 68^{***}$	$271 \pm 50^{***}$	$263 \pm 43^{***}$
CO^{**}	$16 \pm 13^{***}$	No Data	No Data
Total Particulate††	1590	39.8	2.65
Total Organics‡‡	0.6 - 1.0	0.5 - 0.9	0.9 - 1.3
$NO_3^{-\dagger\dagger\dagger}$	0.215 - 0.219	0.003 - 0.006	0.004
$Cl^{-\dagger}$	$3.4 \pm 0.56^{***}$	$4.5 \pm 0.89^{***}$	0.25 - 0.34
$F^{-\dagger}$	$1.3 \pm 0.34^{***}$	$1.2 \pm 0.38^{***}$	$0.033 \pm 0.011^{***}$

* SO_2 was determined by continuous pulsed fluorescence analysis at the air heater inlet and by ultraviolet analysis at the scrubber inlet and outlet (Level 2).

† Primary $SO_4^{=}$ (SO_3 as $SO_4^{=}$ plus particulate sulfate), chloride and fluoride were measured with the CCS (Level 2).

‡ NO_x was determined by continuous chemiluminescent analysis (Level 1).

** CO was determined by non-dispersive infrared analysis (Level 2).

†† Total particulates were determined by SASS measurements (Level 1) and do not include H_2SO_4 aerosol which is a vapor at the collection temperature of 477 K.

‡‡ C_1-C_{16} fractions were determined by gas chromatograph while the $>C_{16}$ fraction was determined gravimetrically (Level 1).

*** Indicated ranges of values represent one standard deviation.

††† Nitrate was determined by extraction of the SASS particulate catch (Level 2).

entirely understood. Primary sulfate (SO_3 as $SO_4^=$ plus particulate sulfate) comprised 0.6% of the flue gas sulfur species at the scrubber inlet and 5% at the scrubber outlet. Primary sulfate at the scrubber inlet and outlet consisted of essentially equal mole fractions of SO_3 and particulate sulfate. However, data from the source assessment sampling system (SASS) indicate particulate sulfate levels of 2.2 and 0.6 ng/J at the scrubber inlet and outlet, respectively, compared to the 10 ng/J levels indicated by the controlled condensation system (CCS). These data may indicate that SO_3 was adsorbing on the particulate filter of the CCS, resulting in inordinately high measured particulate sulfate levels. Because of the large duct width and the proximity of the sampling ports to a right angle bend at the economizer outlet, particulate stratification is probable at the air heater inlet. For this reason, measured primary sulfate levels at the air heater inlet are considered to be low.

Total oxides of nitrogen were determined during a period of 70% boiler load. Because this is nearly the average boiler load, the 265 ng/J emission level should be similar to that of normal operation. Somewhat higher or lower emissions would result from higher or lower load boiler operation.

Carbon monoxide was monitored only at the air heater inlet. While leakage across the air heater may reduce CO levels slightly, neither the ESP nor the scrubber affect flue gas CO levels. Hence, the 16 ng/J CO level measured at the air heater inlet should accurately reflect actual emission levels.

Total particulate data indicate an ESP removal efficiency of 97.5% and a scrubber efficiency of 93.3%; however, the actual ESP removal efficiency probably exceeds 97.5% since particulate stratification apparently resulted in a low particulate catch at the air heater inlet. Particulate at the air heater inlet and scrubber inlet consisted primarily of particles larger than 3μm. At the air heater inlet, 44% of the particulate were larger than 10μm, 42% were 3-10μm, 13% were 1-3μm and 1% were smaller than 1μm. At the scrubber inlet, 25% of the particulate were larger than 10μm, 39% were 3-10μm, 20% were 1-3μm, and 17% were smaller than 1 μm. Only 2% of the particulate emissions to the atmosphere were larger than 3 μm, while 98% were less than 3 μm in diameter. Size distribution data obtained with an MRI impactor indicate that more than

76% of the particulate and H_2SO_4 aerosol emissions to the atmosphere are less than 1 μm in diameter and are capable of deep lung penetration. Sulfate analyses of the impactor plates indicated H_2SO_4 aerosol emissions ranging from 3.7 to 10.4 ng/J with a diameter generally less than 0.5 μm.

Total organic emissions ranged from 0.5 to 1.3 ng/J and consisted primarily of C_1-C_6 organics. The light hydrocarbons were not removed by flue gas processing although decreases in higher molecular weight organics were observed across the ESP and the scrubber. Flue gas processing removed 87% of the C_7-C_{16} organics and 82% of the $>C_{16}$ organics. Higher molecular weight organics were found to consist of aromatics, unsaturated hydrocarbons and either esters or phenols. POMs were not detected at the scrubber inlet or outlet. At the air heater inlet, phenanthrene was detected at 0.7 $\mu g/m^3$ (0.2 pg/J), and fluoranthene and dibenzanthracene were detected at concentrations below 0.6 $\mu g/m^3$ (0.2 pg/J). With the possible exception of dibenzanthracene (which could be dibenz(a,h)anthracene), measured concentrations of these compounds do not appear to pose a hazard to human health.

Inorganic analyses for cations indicated at least 14 elements exceeded their respective Discharge Multimedia Environmental Goal (DMEG) levels at the air heater inlet while only four elements exceeded their DMEG levels at the scrubber inlet. Elemental concentrations in the flue gas after scrubbing did not exceed DMEG levels nor did they exceed Ambient Multimedia Environmental Goal (AMEG) levels. Hence, with respect to detected cations, flue gas emissions did not pose a health hazard for short term direct exposure or continuous exposure after dispersion.

Specific anion analyses indicated emission levels of NO_3^-, Cl^-, and F^- to be 0.004, 0.25-0.34, and 0.033 ng/J, respectively. DMEG values have not been established for NO_3^-. Concentrations of Cl^- and F^- exceeded their respective DMEG values at the air heater inlet and scrubber inlet although they were both below their DMEG concentrations at the scrubber outlet. Hence, the specific anions analyzed did not appear to pose a health hazard with short term direct exposure.

Elemental concentrations in the clarifier overflow, the only liquid waste discharged from the site, did not exceed health-based DMEG values in any case. Ecology-based DMEG values were exceeded by concentrations of Al, Ca, Cd, Fe, Ni, P, and Pb. However, Ca, Cd, Ni, and Pb are present in the process feedwater from Lake Michigan at concentrations similar to those measured in the clarifier overflow. Elemental concentrations in the prescrubber slurry liquids exceeded health-based DMEG values for B, Cr, and Fe, and exceeded ecology-based DMEG values for numerous elements (notably Al, Cd, Fe, Ni, and P). Concentrations of numerous elements in the thiosulfate purge liquids and melt tank liquor exceeded DMEG values.

Organics in the liquid waste streams consisted primarily of $>C_{16}$ compounds. C_7- C_{16} organic concentrations in liquid wastes were generally below the detection limit of 0.001 g/m^3. Total organic concentrations in the prescrubber slurry liquids and clarifier overflow were 0.351-0.361 g/m^3 and 0.108-0.117 g/m^3, respectively. Organics were present in the process feedwater from Lake Michigan at a concentration of 0.235-0.242 g/m^3. No POMs were detected in liquid wastes or process water streams.

Solid waste streams (fly ash, prescrubber solids and ash pond sludge) each contained four to six elements at concentrations exceeding health-based DMEG values and 11 or 12 elements at concentrations exceeding ecology-based DMEG values. Elements of primary concern included Al, As, Fe, Ni, and P. Solids present in the thiosulfate purge and melt tank liquor appear to be relatively pure Na_2SO_3 and $NaHSO_3$, respectively. Elemental impurities present in the soda ash and product sulfur streams did not exceed 265 mg/kg, and most elements were present at levels below 10 mg/kg.

Organics in the fly ash and ash pond sludge consisted primarily of high molecular weight compounds; C_7-C_{16} organics were present at concentrations of 0.345 and 0.245 mg/kg, respectively, while $>C_{16}$ organics were present at concentrations of 4.42 and 4.48 mg/kg, respectively. Solid wastes were found to contain saturated hydrocarbons, aromatics, esters, and ethers. Additionally, the fly ash contained ketones, and the ash pond sludge contained unsaturated hydrocarbons and alcohols. POMs were not detected in fly ash or ash pond sludge samples. The average prescrubber slurry solids content was 0.47% and insufficient solids were collected to enable organic analyses.

3. SITE DESCRIPTION

Located near the extreme northwest city limit of Gary, Indiana, the Dean H. Mitchell Station fronts on the southern end of Lake Michigan. The station is owned and operated by Northern Indiana Public Service Company (NIPSCO). Four generation units are located at this station, Units 4, 5, 6, and 11; each burns coal as the primary fuel. Unit No. 11 was tested under this program. Placed in service in 1969, this unit has a dry bottom Babcock and Wilcox boiler and is equipped with an American Standard electrostatic precipitator (ESP). In 1976, the unit was retrofitted with a Davy McKee/Wellman-Lord flue gas desulfurization (FGD) unit integrated with an Allied SO_2 to S reduction process. Performance tests were successfully completed in September 1977, and a year of demonstraion tests was started in the same month. During performance testing, the average SO_2 reduction was 91% (design 90%) and particulate emission averaged 17 ng/J. A simplified schematic of Unit No. 11 is presented in Figure 1. Sample acquisition points are indicated in the figure and a listing of samples are presented in Table 2.

3.1 THE BOILER

The Mitchell No. 11 boiler is a balanced draft, dry bottom, wall-fired, radiant boiler manufactured by Babcock and Wilcox(B&W). The maximum continuous steam capacity is 103 kg/s with a corresponding turbo-generator output of 115 MW. Normal output ranges from 46 MW to 115 MW with an average load factor of approximately 80% or 92 MW. The furnace front wall contains 12 B&W circular register burners, each of which has gas-fired burner ignitors. Excess combustion air is normally 19% and increases at low loads.

High volatile bituminous coal, H.V.C. rank, from the Captain Mines No. 6 seam generally fuels Unit No. 11. Typical fuel analyses indicate 13.6% moisture, 9.5% ash, 3.2% sulfur, 0.06% chloride, and a heat content of 25,400 KJ/Kg. Feed coal is pulverized to 77% through 200 U.S. mesh prior to combustion. Pulverizer rejects (pyrites) are combined with bottom ash and sluiced to ash disposal ponds.

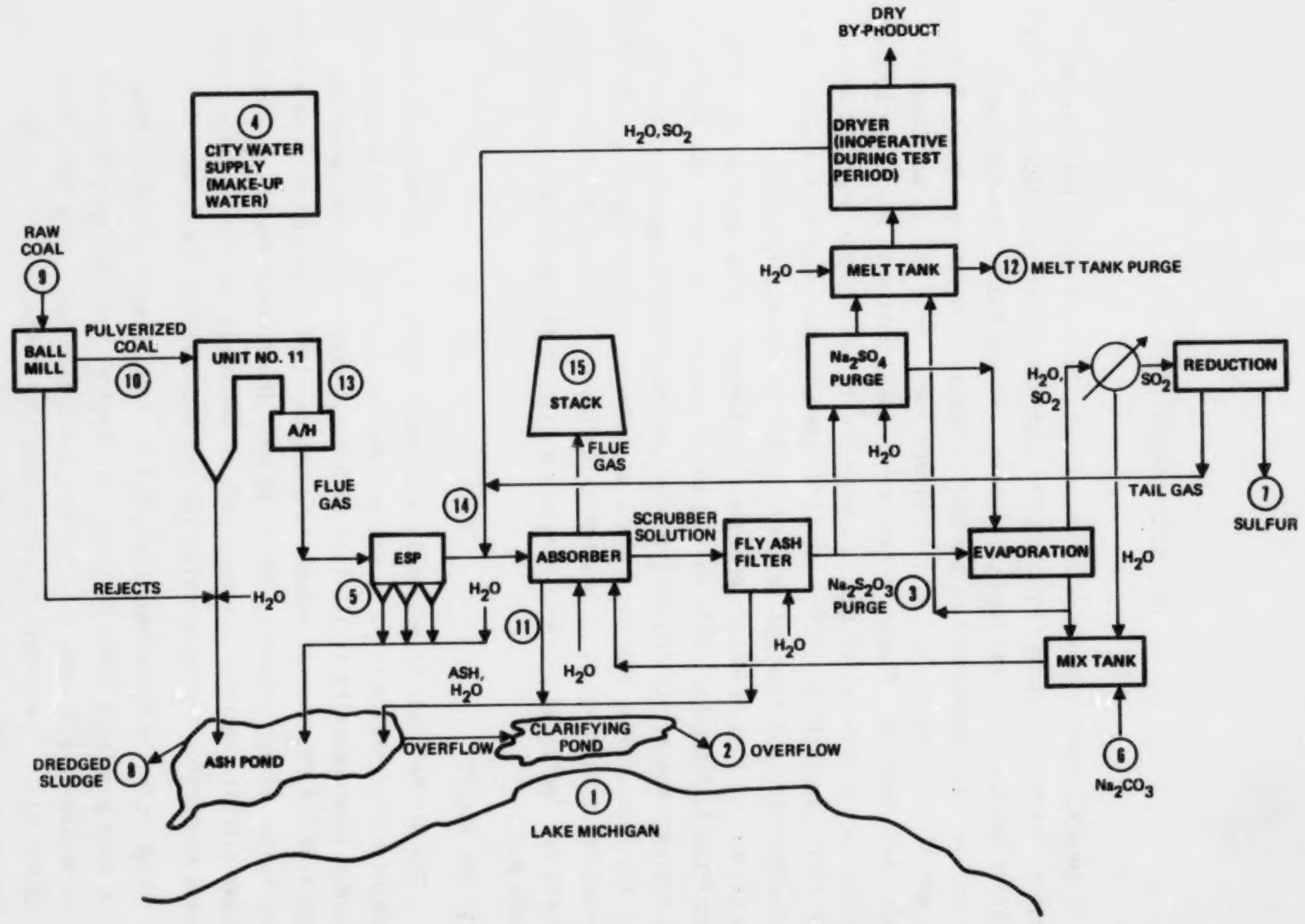
DRY BY-PRODUCT
4 CITY WATER SUPPLY (MAKE-UP WATER)
H_2O, SO_2
DRYER (INOPERATIVE DURING TEST PERIOD)
RAW COAL
9
H_2O
MELT TANK
12 MELT TANK PURGE
BALL MILL
PULVERIZED COAL
10
UNIT NO. 11
13
A/H
15 STACK
Na_2SO_4 PURGE
H_2O
H_2O, SO_2
SO_2
REDUCTION
FLUE GAS
FLUE GAS
14
TAIL GAS
7 SULFUR
SCRUBBER SOLUTION
ESP
ABSORBER
FLY ASH FILTER
EVAPORATION
H_2O
REJECTS
H_2O
5
H_2O
11
$Na_2S_2O_3$ PURGE
3
H_2O
MIX TANK
ASH, H_2O
H_2O
CLARIFYING POND
DREDGED SLUDGE
8
ASH POND
OVERFLOW
2 OVERFLOW
1
LAKE MICHIGAN
6
Na_2CO_3

Figure 1. Schematic of Dean H. Mitchell No. 11 Unit

]

TABLE 2. DEAN H. MITCHELL NO. 11 SAMPLE LISTING

Sample Location	Description
1.	Lake water (normal process water)
2.	Clarifying pond overflow
3.	Thiosulfate purge
4.	City water (backup process water)
5.	Fly ash
6.	Soda ash make-up
7.	Product sulfur
8.	Ash pond sludge
9.	Coarse coal feed
10.	Pulverized coal feed
11.	Prescrubber slurry
12.	Melt tank purge
13.	Flue gas, air heater inlet
14.	Flue gas, scrubber inlet (prior to tail gas addition)
15.	Flue gas, stack effluent

Unit No. 11 has an air energized wall deslagger and retractable soot blower system operated on a programmed daily cycle. The cycle is initiated by the control room operator and requires about two hours to execute. Wall blowers may be actuated independently at any time to maintain steam superheat/reheat temperatures.

Pyrite rejects, bottom ash, and fly ash are sluiced with lake water to one of the three primary ash storage ponds totaling 122,000 m^3 capacity. Solid wastes are thickened and dewatered by means of spillways in the primary storage ponds. Dewatered solid wastes are trucked to off-site disposal areas. Overflow water from the primary settling ponds is clarified in either of two 14,000 m^3 clarification ponds and discharged into the lake. The ash sluicing system combines rejects and bottom ash from the four Mitchell

Station units, and means for obtaining representative samples of these solid wastes from any one unit are not available. Dry fly ash samples may be obtained from the ESP hoppers prior to sluicing.

3.2 ELECTROSTATIC PRECIPITATOR

Particulate emissions from Unit No. 11 are primarily controlled with a cold end, American Standard Co. ESP, which is located between the air heaters and the induced draft fans. The ESP unit employs three electric fields in series. Efficiencies of the first field and the first two fields in combination are 87.7% and 95.6%, respectively. The overall efficiency of the ESP unit is 98.4%. Detailed ESP specifications are presented in Table 3.

3.3 DEMONSTRATION SO_2 RECOVERY SYSTEM

A demonstration SO_2 recovery system capable of processing the full load flue gas output from Unit No. 11 controls SO_2 emissions utilizing a Wellman-Lord scrubber and an Allied Chemical SO_2 reduction process. Principal raw materials utilized by the SO_2 recovery system are natural gas, water, steam, and sodium carbonate. System products are high purity sulfur and, to a lesser extent, a granular sodium sulfate/sulfite mixture. A schematic of the SO_2 recovery system is presented in Figure 2.

Flue gas exhausted from the ESP is passed to the inlet of the turbine driven booster fan. Recycle tail gas from the SO_2 reduction unit is mixed with the flue gas ahead of the booster fan. The fan discharges the gas into the prescrubber section of the absorption system, which serves to cool the gas and scrub residual particulates. The combined gases enter the prescrubber section at about 422 K. The prescrubber is a single-stage, variable throat venturi contactor with a pressure drop of 0.5-1 kPa and a liquid to gas ratio of approximately 0.4 $1/m^3$. A circulation pump draws liquid from the scrubber sump and returns it to the contactor. A mist eliminator is provided at the upper portion of the sump to remove entrained prescrubber liquid from the cooled flue gas. The solids content of the sump liquor is controlled by means of a purge stream which is discharged to the primary ash storage ponds. Make-up water is added to the prescrubber to compensate for losses due to evaporation and fly ash purge.

TABLE 3. MITCHELL NO. 11 PRECIPITATOR SPECIFICATIONS

Design Flow Rate	194 m^3/s
Temperature	416K
Inlet Particulate Loading	8 to 15 g/m^3(STD)
Pressure Drop	100 Pa
Removal Efficiency	98.4%
Rate Constant	1.7 m/s
Plate area	5,411 m^2
Treatment Length	5.27 m
# Fields	3
# Ducts	56 (@ 0.23 m)
Wire Ft.	40,320 (@ 0.18 m)
Treatment Time	3.2 sec
Delivery	July 1969
# Plate Rappers	32
# Wire Vibrators	12
Hopper Ash Capacity Minimum	8 hrs.
# Bus Sections	6
Plate Height	9.1 m
Energization	Half Wave

Provisions in the unit for another field, 1.8 m treatment length above hopper can be added later

Expected removal w/field #1 only 87.7%

Expected removal w/fields #1 - 2 only 95.6%

Expected hopper #3 collects 2.8% of the dust

Ash removal pneumatically by 3 lines (fields 1, 2, 3)

No. ash hoppers - 12

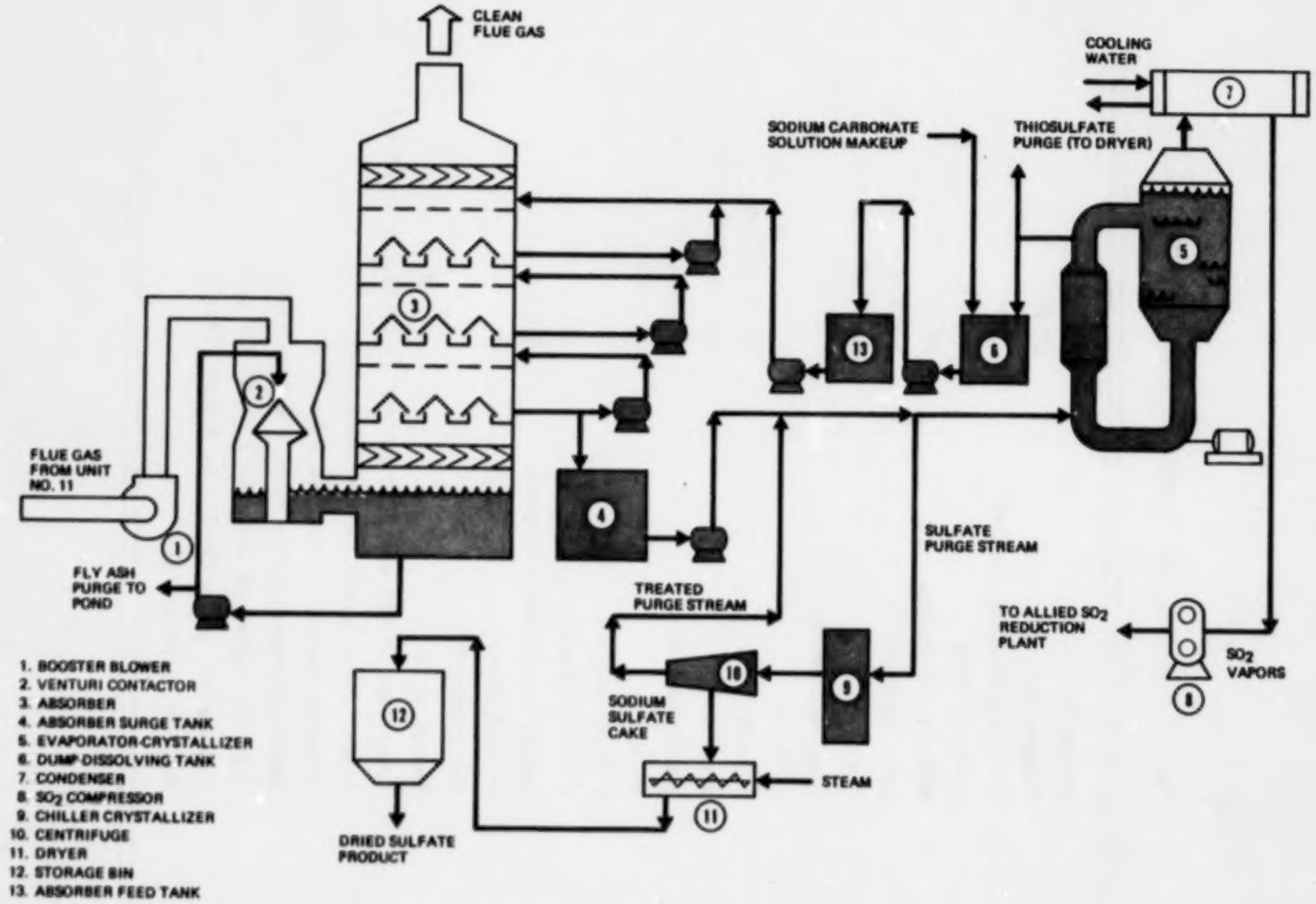
CLEAN FLUE GAS
COOLING WATER
SODIUM CARBONATE SOLUTION MAKEUP
THIOSULFATE PURGE (TO DRYER)
FLUE GAS FROM UNIT NO. 11
FLY ASH PURGE TO POND
SULFATE PURGE STREAM
TREATED PURGE STREAM
TO ALLIED SO_2 REDUCTION PLANT
SO_2 VAPORS
SODIUM SULFATE CAKE
STEAM
DRIED SULFATE PRODUCT
1. BOOSTER BLOWER
2. VENTURI CONTACTOR
3. ABSORBER
4. ABSORBER SURGE TANK
5. EVAPORATOR-CRYSTALLIZER
6. DUMP-DISSOLVING TANK
7. CONDENSER
8. SO_2 COMPRESSOR
9. CHILLER CRYSTALLIZER
10. CENTRIFUGE
11. DRYER
12. STORAGE BIN
13. ABSORBER FEED TANK

Figure 2. Schematic of the Wellman-Lord SO_2 Recovery System

The absorber section contains three contact stages in series for countercurrent SO_2 absorption. Each stage consists of a valve tray and a collector tray, and has its own liquid recirculation system to promote good gas-liquid contact. The pressure drop across the absorber is 2.5-3 kPa with a liquid to gas ratio of approximately 1.6 l/m^3. The absorption process proceeds at about 327 K. Fresh scrubber solution is fed from the absorber feed tank to the top contact stage. A mist eliminator is provided at the top of the unit to remove entrained scrubber solution from the treated flue gas. Reduced in SO_2 content with each successive contact stage, the flue gas passes upward through the absorber stages and mist eliminator, and is exhausted from the system.

Reaction between SO_2 and the soda ash based, sodium sulfite scrubber solution produces sodium bisulfite (Equation 1). However, limited reaction with O_2 or SO_3 converts 4% or less of the flue gas sulfur to sodium sulfate (Equations 2 and 3). Sodium sulfate is non-reactive and is, therefore, purged from the system. These reactions may be represented as follows:

$$SO_2 + Na_2SO_3 + H_2O \rightarrow 2NaHSO_3 \quad (1)$$

$$O_2 + 2Na_2SO_3 \rightarrow 2Na_2SO_4 \quad (2)$$

$$SO_3 + 2Na_2SO_3 + H_2O \rightarrow Na_2SO_4 + 2NaHSO_3 \quad (3)$$

To reduce the quantity of purge and, therefore, soda ash make-up, the purge treatment system subjects part of the spent scrubber solution to a fractional crystallization process. Crystals rich in Na_2SO_4 are produced by chilling the purge stream. Product crystals are recovered by centrifugation, combined with a sodium thiosulfate purge stream from the evaporator, and dried for sale or disposal. This treatment concentrates the recoverable sulfur compounds, Na_2SO_3 and $NaHSO_3$, in the liquor. The treated liquor enters the evaporator for SO_2 recovery.

Spent scrubber solution and purified solution from the sulfate purge system enter an evaporator unit for solution regeneration and SO_2 recovery. The evaporator is a single effect, forced-circulation vacuum evaporation unit. Heat is provided with a steam heat exchanger, and the clean condensate is recycled to the boiler system. Heat supplied to the bisulfite solution causes decomposition to SO_2, H_2O, and crystalline Na_2SO_3, by the following reaction:

$$2NaHSO_3 \rightarrow Na_2SO_3 + SO_2 + H_2O \qquad (4)$$

Small amounts of sodium sulfate and thiosulfate are also produced during solution regeneration. The side reaction producing sulfates and thiosulfates is as follows:

$$6NaHSO_3 \rightarrow 2Na_2SO_4 + Na_2S_2O_3 + 2SO_2 + 3H_2O \qquad (5)$$

Thiosulfate buildup is controlled by purging a portion of the regenerated solution; the purge stream is subsequently dried for sale or disposal.

Vapor products of thermal decomposition, SO_2 and H_2O, are exhausted from the evaporator and enter a primary condenser. Primary condensate passes through a condensate stripper and into an agitated dissolving tank. Sulfite slurry withdrawn from the evaporator circulating loop is also charged to the dissolving tank. The resulting solution enters the absorber top stage via the absorber feed tank.

Vapors from the primary condenser enter the secondary condenser along with stripper overhead vapor. Secondary condensate returns to the stripper. Outlet gas, rich in SO_2, is compressed and sent to the Allied SO_2 reduction unit.

To replace sodium lost with the sulfate and thiosulfate purge, soda ash is fed to the agitated dissolving tank. Soda ash reacts with sodium bisulfite to produce sodium sulfite by the following reaction:

$$Na_2CO_3 + 2NaHSO_3 \rightarrow 2Na_2SO_3 + CO_2 + H_2O \qquad (6)$$

Reduction of the concentrated SO_2 stream is accomplished in a two-stage process employing partial reduction of SO_2 with methane (natural gas) using a catalyst to produce sulfur vapor and hydrogen sulfide, followed by a secondary Claus conversion system in which the H_2S reacts with the remaining SO_2 to produce additional sulfur. During primary reaction, approximately half of the input SO_2 is reduced to sulfur by direct reaction with the reductant:

$$2SO_2 + CH_4 \rightarrow CO_2 + 2H_2O + S_2 \qquad (7)$$

Simultaneously, a major portion of the remaining SO_2 is converted into hydrogen sulfide and additional sulfur by the reaction:

$$3SO_2 + 2CH_4 \rightarrow 2CO_2 + 2H_2O + 2H_2S + 1/2\ S_2 \qquad (8)$$

The gas flow rates and operating conditions in the primary reaction system are carefully controlled so that the mixture of H_2S and unconverted SO_2 in the product gases from the primary reaction system closely approximates the two-to-one molar ratio required for the subsequent Claus reaction:

$$2H_2S + SO_2 \rightarrow 2H_2O + 3/2\ S_2 \qquad (9)$$

The Claus tail gases contain residual hydrogen sulfide and carbon sulfides, which are oxidized to SO_2 by incineration using air-methane combustion. Hot incinerator gases are recycled to the Wellman-Lord scrubber for sulfur oxide removal before venting to atmosphere.

4. COMPREHENSIVE EMISSIONS ASSESSMENT

Multi-media emission tests were conducted on Boiler No. 11 of the Dean H. Mitchell station from 24 August through 13 September 1979. Gaseous, liquid, and solid emissions were sampled during normal boiler operation to obtain assessment data. Flue gas sampling was conducted before the air heater inlet and before and after the scrubber to determine which pollutants are removed or modified by the control devices. Selected liquid and solid samples were also obtained as previously specified in Table 2. This section details plant operating conditions during the test period, describes the tests performed and presents test results and data evaluation.

4.1 TEST CONDITIONS

The test period consisted of eight test days. Details of the boiler operating conditions during testing are presented in Table 4. Boiler loads ranged from 79 to 90 MW which corresponds to between 69 and 78% of full load operation. Average fuel feed and steam production rates ranged from 34.5 to 36.9 Mg/hr and 250 to 313 Mg/hr, respectively. However, tabulated fuel feed and steam production rates are nominal and the true accuracy of these values is not known. Plant personnel indicated that fuel feed rates are accurate to within approximately 3%. Monitored fuel feed rates were found to fluctuate by 0.5 to 4.4% during tests. Energy balances based upon fuel feed and steam production data obtained during the test period, and nominal enthalpy and steam partitioning data cited in the Demonstration Test Plan (1) indicate that measured fuel feed and steam production rates are accurate to within about 17% or better. Measured fuel feed rates were found to be high with respect to measured steam production rates, although the source of this discrepancy cannot be identified based upon available data. The overall boiler efficiency computed from gross electrical output and fuel feed rates was approximately 30% during the test period. Furnace oxygen concentrations, measured at the air heater inlet, ranged from 2.0 to 4.8%; the corresponding excess air based upon fuel ultimate analysis ranged from 10 to 29%.

TABLE 4. SUMMARY OF TEST CONDITIONS

Test Date	Gross Electrical Output, MW	Percent of Maximum Load	Fuel Feed Rate*, kg/hr	Steam Production Rate, 10^5 kg/hr	Overall Efficiency†, %	Average O_2 at the Air Heater Inlet, %	Estimated Excess Air at Furnace‡, %	Flue Gas Flow Rate, dscm/s**
8-24	80	70	35,250	2.59	29.6	4.8	29.0	92.3
8-28	79	69	34,470	2.50	29.9	4.3	25.2	87.0
8-29	79	69	34,560	2.63	29.8	3.1	17.0	81.4
8-30	80	70	35,020	2.69	29.8	2.5	13.2	79.8
9-06	90	78	No Data	3.13	No Data	2.0	10.3	No Data
9-11	85	74	36,250	3.13	30.6	3.7	21.0	88.2
9-12	83	72	35,990	2.81	30.1	3.4	18.9	86.3
9-13	85	74	36,920	2.72	30.0	3.5	19.6	89.0

* Fuel feed rates fluctuated by 0.5-4.4% during testing.

† Efficiency is computed from the gross electrical output and nominal fuel feed rates.

‡ Percentage excess air is estimated from the ultimate analysis of the fuel and O_2 concentrations measured at the air heater inlet.

** Flue gas flow rates are based on O_2 levels at the air heater inlet.

Tabulated flue gas flow rates were computed from fuel feed rate data and ultimate fuel analysis using the following expression:

$$n_{FG} = \frac{4.762\ (n_C + n_S + 0.45\ n_N) + 0.9405\ n_H - 3.762\ n_{O_2}}{1 - 0.04762\ O_2}$$

where:

n_{FG} = gram moles of dry effluent per gram of fuel
n_j = gram moles of element j per gram of fuel
O_2 = volume percent O_2 in the flue gas

Flue gas flow rates are expressed as dry standard cubic meters per second based upon O_2 concentrations measured at the air heater inlet; standard temperature and pressure are defined as 293 K and 101.3 kPa, respectively. It should be noted that flue gas flow rates change during processing as a result of air leakage. For example, flow rates at the scrubber inlet can be estimated by correcting tabulated flow rate values to 7% O_2.

Raw and pulverized coal samples were obtained each day of testing. Raw, crushed coal samples at a top-size of approximately 20 mm were obtained once daily from the storage bin outlets. Pulverized coal (70% below 200 mesh) was sampled on a continuous basis downstream of the pulverizers. Raw and pulverized coal samples were each composited during the test period. Analyses of composite samples are presented in Table 5 and indicate good agreement. Slight discrepancies in analyses are attributed primarily to differences in sampling methodologies; analyses of the pulverized coal sample are considered to be most representative of the feed during the test period because of ease of sampling fine coal and the continuous sampling method. The fuel feed to Unit No. 11 is reasonably uniform since NIPSCO's coal procurement department has previously negotiated for a consistent supply to ensure uniform boiler and FGD system operation. For example, unpublished analyses obtained in conjunction with extended demonstration operation of the FGD system indicate that fuel sulfur may have fluctuated by approximately 7% during the test period.

Elemental analyses of the composite fuel samples are presented in Table 6. Raw and pulverized coal analyses are in good agreement for most elements, although concentrations of calcium, potassium, magnesium, manganese, lead, and zinc were somewhat lower in the pulverized coal than in the raw coal. Again, pulverized coal sample is considered to be most representative of the feed during the test period.

TABLE 5. SUMMARY OF FUEL ANALYSES*

Component	Raw Coal	Pulverized Coal
Moisture, %	7.59	3.92
Ash, %	11.93	12.50
Volatile, %	40.06	39.11
Fixed Carbon, %	48.01	48.39
Total Carbon, %	69.48	68.98
Hydrogen, %	4.76	4.58
Nitrogen, %	1.40	1.43
Chlorine, %	0.04	0.03
Sulfur, %	3.77	3.52
Oxygen†, %	8.62	8.96
Heating Value, kJ/kg	29,071	28,762

* All analyses are on a dry basis except fuel moisture.

† Oxygen concentrations are determined by difference.

4.2 TESTS AND FIELD ANALYSES

Gaseous, liquid, and solid samples obtained during the test effort were analyzed in the field and/or in the laboratory, as required. This section briefly describes the tests and field analyses which were performed. The methods and procedures used during this study are, in some instances, modified Level 1 sampling and/or analysis procedures and are documented in the manual "Emissions Assessment of Stationary Combustion Systems: Methods and Procedures Manual for Sampling and Analysis", January 1979 (2). The Level 2 methods and procedures included "state-of-the-art" techniques as adapted to the needs of this site. Details of these procedures are presented in the Appendices.

TABLE 6. ELEMENTAL ANALYSES OF RAW AND PULVERIZED COAL*

Element	Concentration in Coal, µg/g	
	Raw Coal	Pulverized Coal
Al	11,200	7,170
As	<4	<4
Ba	0.38	<1.4
Be	<0.04	<0.05
Ca	1,540	436
Cd	<0.3	<0.3
Co	<0.4	<0.4
Cr	<0.4	<0.5
Cu	11	11
Fe	16,400	14,400
Ga	<3	<3
Hg	<1	<1
K	543	240
La	<0.01	<0.01
Li	8	9
Mg	170	50
Mn	27	7.1
Na	297	289
Ni	36	19
Pb	25	6.7
P	115	97
Sb	<17	<19
Si	23,140	27,300
Sn	<4	<5
Sr	<3	<3
Ti	<0.08	<0.1
V	41	33
Zn	135	38
Zr	29	32

* Elemental concentrations were determined by inductively coupled plasma optical emission spectroscopy (ICP) analysis (Level 2).

4.2.1 Gaseous Effluents

A schedule of flue gas testing is presented in Table 7. The Source Assessment Sampling System (SASS) was used to collect gaseous and particulate emission samples at the air heater inlet, scrubber inlet and scrubber outlet. The SASS train is illustrated in Figure 3. The train consists of a heated probe, three cyclones and a filter in a heated oven. The 10 and 1 μm cyclones were not used at the scrubber outlet because of the low particulate loading at this point. The remainder of the system consists of a gas conditioning system, an XAD-2 polymer adsorbent trap and a series of impingers. The polymer absorbs gaseous organics and some inorganics, and the impingers collect the remaining inorganics. All sample contact surfaces are Type 316 stainless steel, teflon or glass. Thirty cubic meters of flue gas were collected during Level 1 SASS operation at the air heater inlet. To provide for bioassy test requirements in addition to Level 1 SASS requirements, 114 and 125 m^3 were collected at the scrubber inlet and outlet, respectively.

Integrated bag samples were obtained from each flue gas sampling point during SASS operation. These samples were utilized to determine concentrations of C_1-C_6 hydrocarbons by a Shimadzu GC-Mini 1 gas chromatograph with flame ionization detectors. Oxygen, CO, CO_2, and N_2 were also determined in bag samples using a Shimadzu GC-3BT chromatograph with thermal conductivity detectors.

Continuous monitor data were obtained using two separate monitor systems during the test period. Data from the air heater inlet were obtained using equipment brought on site specifically for this test effort. Data from the scrubber inlet and outlet were obtained using the continuous monitor system installed on site for previous acceptance and demonstration testing of the FGD system. A listing of the monitoring equipment associated with these two system is presented in Table 8. It should be noted that the monitor system for the air heater inlet was preceeded by a gas conditioner to remove moisture prior to gas analysis. The monitor system for the scrubber inlet and outlet employed gas conditioning subsequent to SO_2 and NO_x analyses but prior to O_2, CO_2. amd CO analyses; hence, a correction for flue gas moisture was applied to measured SO_2 and NO_x data.

Additional Level 2 sampling involved the controlled condensation system (CCS) and MRI impactors. A glass CCS, as shown in Figure 4, was used at each location to obtain samples for SO_2, SO_3 (as H_2SO_4), particulate sulfate, HCl

TABLE 7. FLUE GAS TEST PERFORMANCE SCHEDULE

Test Date	Location	Sampling/Analyses Performed					
		Level 1, SASS	Level 1/ Bioassay SASS	Level 1, C_1-C_6 Hydrocarbons	Levels 1 and 2, Continuous O_2, SO_2, NO_x, CO, CO_2	Level 2, CCS	Level 2, MRI
8-24	Air heater inlet						
	Scrubber inlet		X	X	X		
	Scrubber outlet		X	X	X		
8-28	Air heater inlet	X		X	X		
	Scrubber inlet		X	X	X		
	Scrubber outlet		X	X	X		
8-29	Air heater inlet	X		X	X		
	Scrubber inlet		X	X	X		
	Scrubber outlet		X	X	X		
8-30	Air heater inlet						
	Scrubber inlet		X	X	X		
	Scrubber outlet		X	X	X		
9-06	Air heater inlet				X*	X	
	Scrubber inlet				X*	X	
	Scrubber outlet				X*	X	
9-11	Air heater inlet				X*	X	
	Scrubber inlet				X*	X	X
	Scrubber outlet				X*	X	X
9-12	Air heater inlet				X*	X	
	Scrubber inlet				X*	X	X
	Scrubber outlet				X*	X	X
9-13	Air heater inlet				X*		
	Scrubber inlet				X*		X
	Scrubber outlet				X*		X

* During controlled condensation system (CCS) and MRI impactor testing, only O_2, SO_2, and CO_2 were monitored continuously.

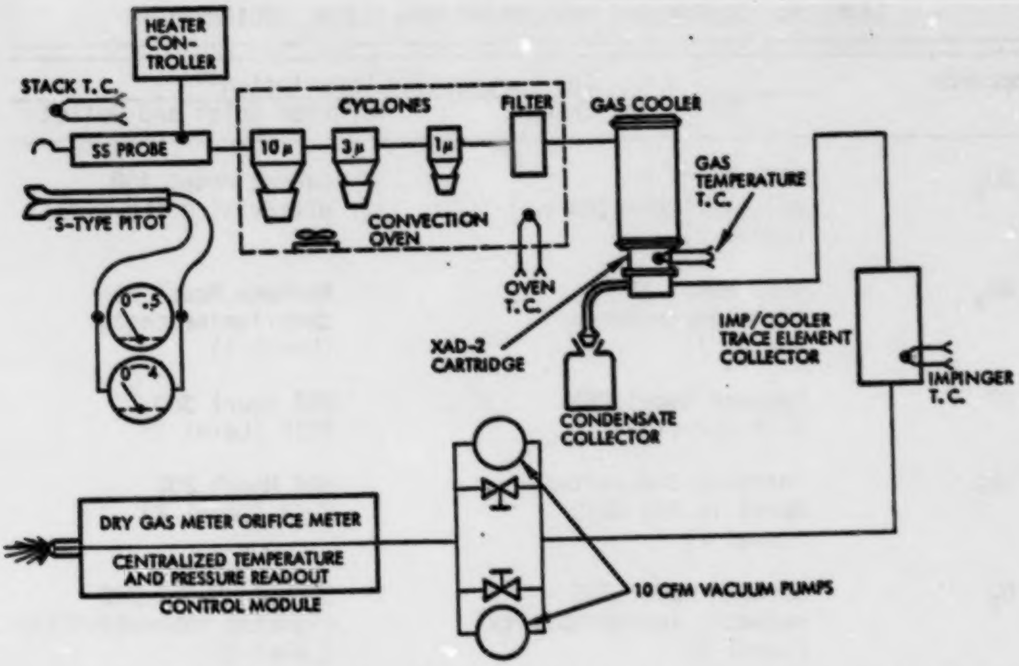
HEATER CON-TROLLER
STACK T.C.
SS PROBE
CYCLONES
10 μ
3 μ
1 μ
FILTER
GAS COOLER
GAS TEMPERATURE T.C.
S-TYPE PITOT
CONVECTION OVEN
OVEN T.C.
XAD-2 CARTRIDGE
CONDENSATE COLLECTOR
IMP/COOLER TRACE ELEMENT COLLECTOR
IMPINGER T.C.
0 .5
0 4
DRY GAS METER ORIFICE METER
CENTRALIZED TEMPERATURE AND PRESSURE READOUT
CONTROL MODULE
10 CFM VACUUM PUMPS

Figure 3. Schematic of the Source Assessment Sampling System (SASS)

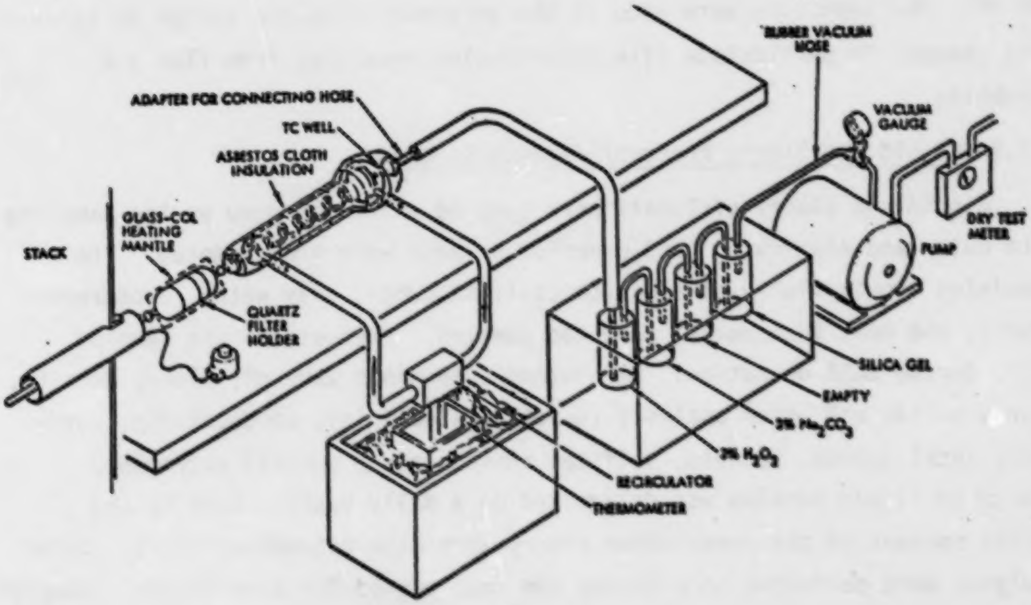
RUBBER VACUUM HOSE
ADAPTER FOR CONNECTING HOSE
TC WELL
ASBESTOS CLOTH INSULATION
VACUUM GAUGE
GLASS-COL HEATING MANTLE
STACK
QUARTZ FILTER HOLDER
DRY TEST METER
PUMP
SILICA GEL
EMPTY
3% Na_2CO_3
3% H_2O_2
RECIRCULATOR
THERMOMETER

Figure 4. Schematic of Modified Controlled Condensation System (CCS)

TABLE 8. CONTINUOUS MONITORING ANALYTICAL EQUIPMENT

Compounds	Instrumentation Description	
	Air Heater Inlet	Scrubber Inlet and Outlet
SO_2	TECO Model 40 pulsed fluorescence (Level 2)	DuPont Model 400 ultraviolet (Level 2)
NO_x	TECO Model 10 chemiluminescence (Level 1)	Beckman Model 955 chemiluminescence (Level 1)
CO	Beckman Model 865 NDIR (Level 2)	MSA Model 300 NDIR (Level 2)
CO_2	Infrared Industries Model IR 702 NDIR (Level 2)	MSA Model 202 NDIR (Level 2)
O_2	Beckman Model 755 magnetic susceptibility (Level 2)	Beckman Model 742 magnetic susceptibility (Level 2)

and HF. MRI impactors were used at the scrubber inlet and outlet to determine changes in particulate size distribution resulting from flue gas scrubbing.

4.2.2 Liquid and Slurry Process/Effluent Streams

Liquid and slurry effluents were sampled either by grab or tap sampling. Lake water and clarifying pond overflow streams were grab sampled. The remaining liquid/slurry streams (thiosulfate purge, city water, prescrubber slurry, and melt tank purge) were tap sampled. Each stream was sampled daily during SASS operation. Parameters determined were pH, slurry density, slurry solids and water analyses (acidity, alkalinity, conductivity, hardness, total solids, sulfate, sulfite, phosphate and ammonia nitrogen). The pH of liquid samples was determined on a daily basis. Density and solids content of the prescrubber slurry were also determined daily. Water analyses were performed once during the test period for each stream. Samples from each stream were generally composited prior to laboratory analysis.

4.2.3 Solid Process/Effluent Streams

Both grab sampling and continuous sampling were employed to obtain solid samples of process/effluent streams. Fly ash, soda ash, coarse coal, and product sulfur samples were obtained by grab sampling. Pulverized coal samples were obtained on a continuous basis. No field analyses of solid samples were required.

4.3 LABORATORY ANALYSES

Samples submitted for laboratory analysis were processed through one of four basic analytical schemes: 1) the analytical scheme for particulates and gases; 2) the analytical scheme for solids, liquids, and slurries; 3) the CCS sample analysis scheme; or 4) the MRI impactor sample analysis scheme. The principal elements of these analytical schemes are presented in Figures 5 through 7. Detailed analytical procedures can be found in the manual "Emissions Assessment of Conventional Stationary Combustion Systems: Methods and Procedures Manual for Sampling and Analysis", January 1979 (2). A discussion of procedural modifications specific to this test effort is presented in the Appendices.

4.4 FLUE GAS EMISSIONS

4.4.1 Criteria Pollutants

As discussed previously, concurrent Level 1 and Level 2 testing comprised four test days. Measured criteria pollutant emissions for these tests are summarized in Table 9 with the exception of lead which will be discussed in a subsequent section. Daily averages of criteria pollutant emissions data are presented in Table 10. Additionally, average uncontrolled emissions are compared with the EPA AP-42 emission factors for uncontrolled sources (3) in Table 11. Emissions data are discussed by specific pollutant in the ensuing subsections.

Sulfur Dioxide--

Uncontrolled SO_2 emissions were measured in the range of 1710 to 2750 ng/J. Average uncontrolled SO_2 emissions at the air heater inlet and scrubber inlet were 1968 and 2482 ng/J, respectively. These values may be compared with a computed SO_2 emission factor of 2399 ng/J based on fuel

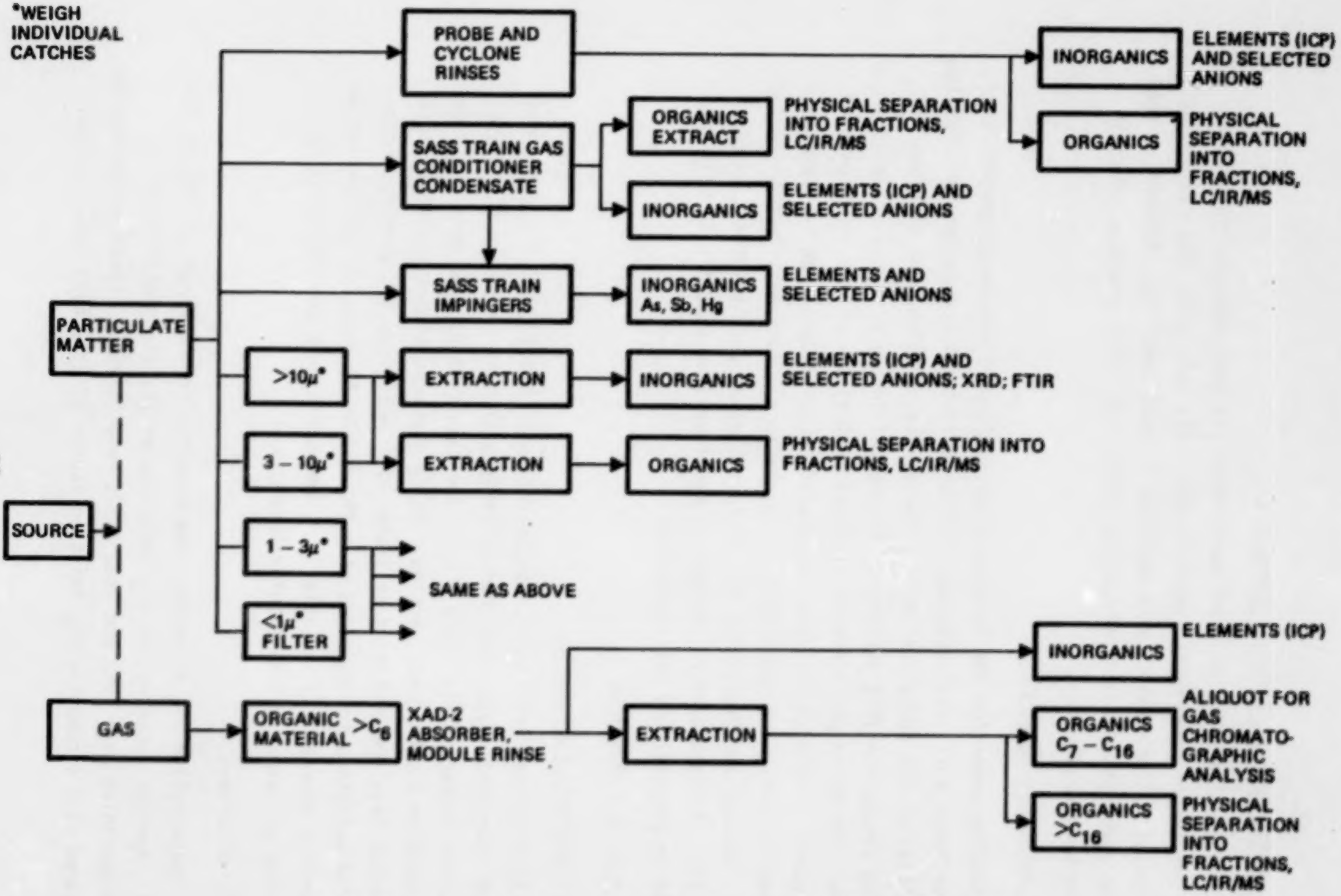
*WEIGH INDIVIDUAL CATCHES
PARTICULATE MATTER
SOURCE
GAS
PROBE AND CYCLONE RINSES
SASS TRAIN GAS CONDITIONER CONDENSATE
SASS TRAIN IMPINGERS
>10μ*
3 – 10μ*
1 – 3μ*
<1μ* FILTER
EXTRACTION
EXTRACTION
SAME AS ABOVE
ORGANICS EXTRACT
PHYSICAL SEPARATION INTO FRACTIONS, LC/IR/MS
INORGANICS
ELEMENTS (ICP) AND SELECTED ANIONS
INORGANICS As, Sb, Hg
ELEMENTS AND SELECTED ANIONS
INORGANICS
ELEMENTS (ICP) AND SELECTED ANIONS; XRD; FTIR
ORGANICS
PHYSICAL SEPARATION INTO FRACTIONS, LC/IR/MS
INORGANICS
ELEMENTS (ICP) AND SELECTED ANIONS
ORGANICS
PHYSICAL SEPARATION INTO FRACTIONS, LC/IR/MS
ORGANIC MATERIAL >C6
XAD-2 ABSORBER, MODULE RINSE
EXTRACTION
INORGANICS
ELEMENTS (ICP)
ORGANICS C7 – C16
ALIQUOT FOR GAS CHROMATOGRAPHIC ANALYSIS
ORGANICS >C16
PHYSICAL SEPARATION INTO FRACTIONS, LC/IR/MS

Figure 5. Basic Analytical Scheme for Particulate and Gases

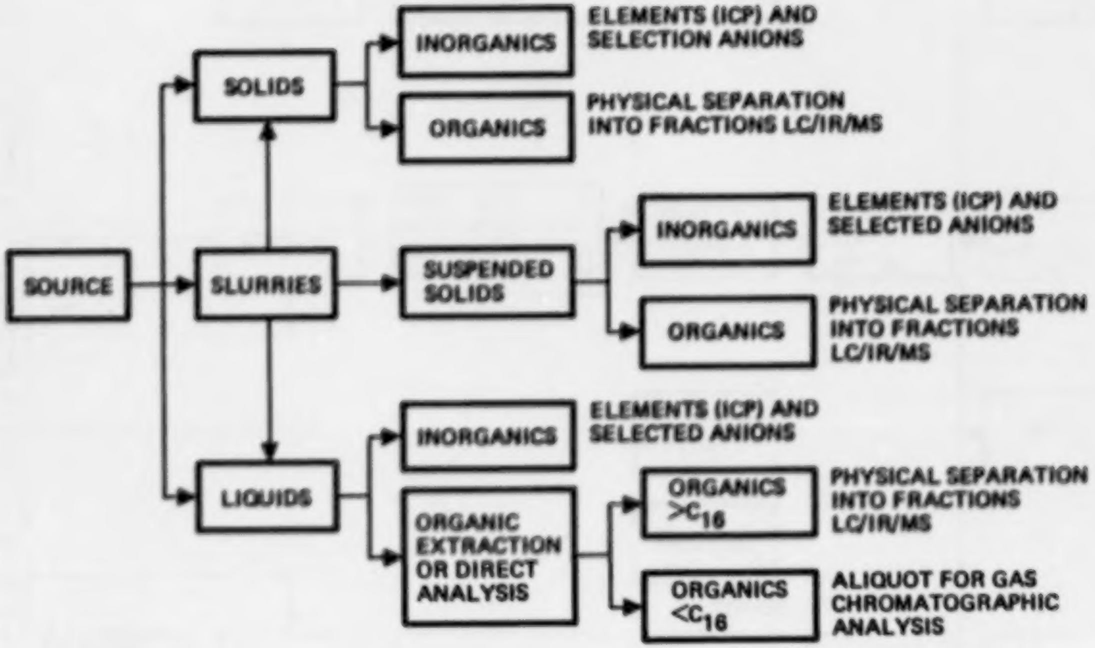
SOURCE
SOLIDS
SLURRIES
LIQUIDS
INORGANICS
ELEMENTS (ICP) AND SELECTION ANIONS
ORGANICS
PHYSICAL SEPARATION INTO FRACTIONS LC/IR/MS
SUSPENDED SOLIDS
INORGANICS
ELEMENTS (ICP) AND SELECTED ANIONS
ORGANICS
PHYSICAL SEPARATION INTO FRACTIONS LC/IR/MS
INORGANICS
ELEMENTS (ICP) AND SELECTED ANIONS
ORGANIC EXTRACTION OR DIRECT ANALYSIS
ORGANICS >C16
PHYSICAL SEPARATION INTO FRACTIONS LC/IR/MS
ORGANICS <C16
ALIQUOT FOR GAS CHROMATOGRAPHIC ANALYSIS

Figure 6. Basic Analytical Scheme for Solids, Slurries, and Liquids

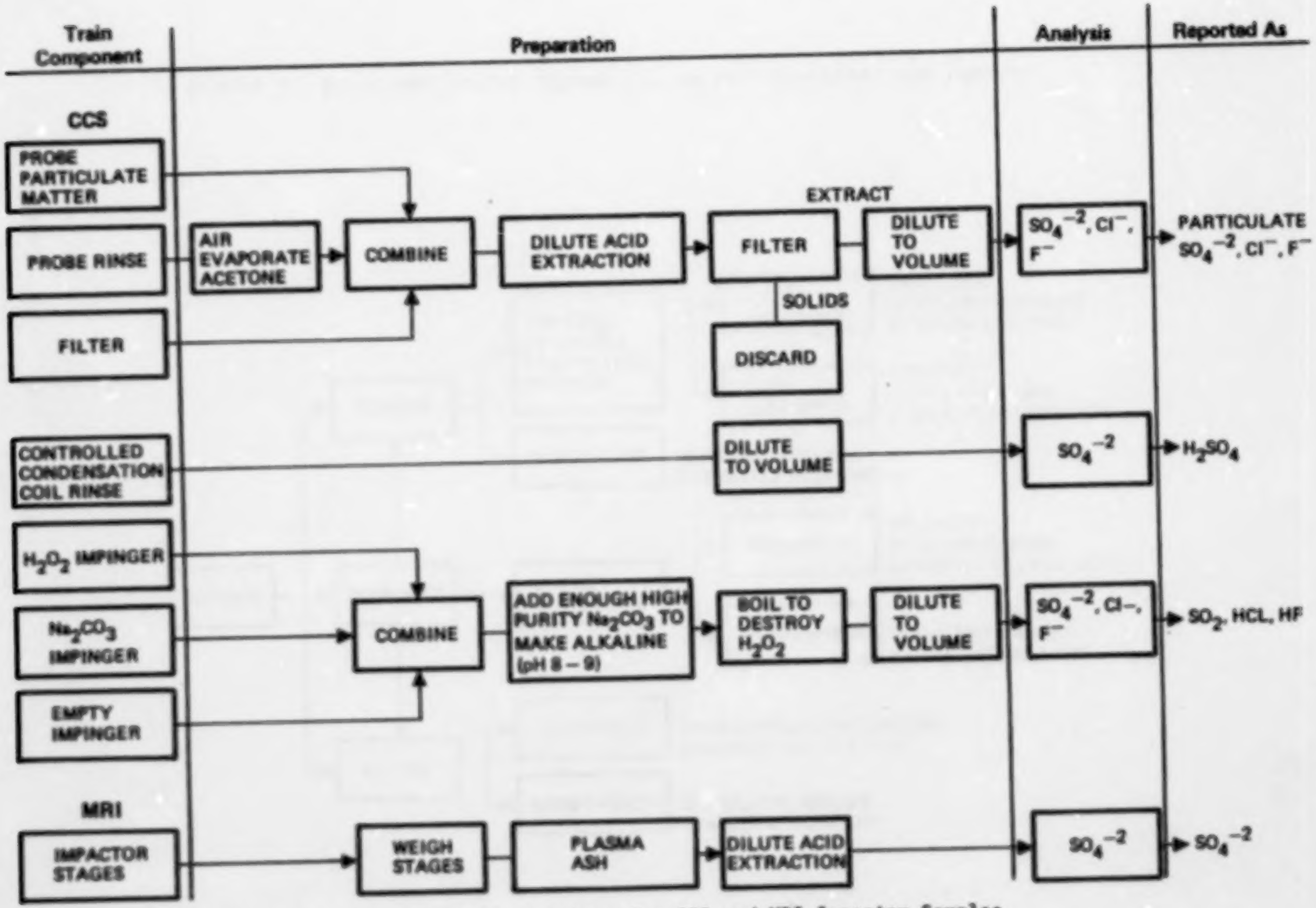
Train Component
Preparation
Analysis
Reported As
CCS
PROBE PARTICULATE MATTER
PROBE RINSE
FILTER
AIR EVAPORATE ACETONE
COMBINE
DILUTE ACID EXTRACTION
FILTER
EXTRACT
DILUTE TO VOLUME
SOLIDS
DISCARD
SO_4^{-2}, Cl^-, F^-
PARTICULATE SO_4^{-2}, Cl^-, F^-
CONTROLLED CONDENSATION COIL RINSE
DILUTE TO VOLUME
SO_4^{-2}
H_2SO_4
H_2O_2 IMPINGER
Na_2CO_3 IMPINGER
EMPTY IMPINGER
COMBINE
ADD ENOUGH HIGH PURITY Na_2CO_3 TO MAKE ALKALINE (pH 8 – 9)
BOIL TO DESTROY H_2O_2
DILUTE TO VOLUME
SO_4^{-2}, Cl–, F^-
SO_2, HCL, HF
MRI
IMPACTOR STAGES
WEIGH STAGES
PLASMA ASH
DILUTE ACID EXTRACTION
SO_4^{-2}
SO_4^{-2}

Figure 7. Basic Analytical Scheme for CCS and MRI Impactor Samples

TABLE 9. AVERAGE MEASURED CRITERIA POLLUTANT EMISSIONS

Pollutant	Emission Factor, ng/J		
	Air Heater Inlet	Scrubber Inlet	Scrubber Outlet
SO_2[*]	1968 ± 145[‡‡]	2482 ± 158[‡‡]	266 ± 39[‡‡]
NO_x[†] (as NO_2 at 70% load)	224 ± 68[‡‡]	271 ± 50[‡‡]	263 ± 43[‡‡]
CO[‡]	16 ± 13[‡‡]	No Data	No Data
Total Particulate[**]	1590	39.8	2.65
Total Organics[††]	0.6 - 1.0	0.5 - 0.9	0.9 - 1.3

[*] SO_2 was determined by continuous pulsed fluorescence analysis at the air heater inlet and by ultraviolet analysis at the scrubber inlet and outlet (Level 2).

[†] NO_x was determined by continuous chemiluminescent analysis (Level 1).

[‡] CO was determined by non-dispersive infrared analysis (Level 2).

[**] Total particulates were determined by SASS measurements (Level 1).

[††] C_1- C_{16} fractions were determined by gas chromatograph while the $>C_{16}$ fraction was determined gravimetrically (Level 1).

[‡‡] Indicated ranges of values represent one standard deviation.

analyses and an assumed conversion of 98% fuel sulfur to SO_2; this factor is in good agreement with the AP-42 emission factor of 2300 ng/J. The average SO_2 level measured at the scrubber inlet is in good agreement with the anticipated level. However, the average SO_2 level measured at the air heater inlet appears to be low by 18%.

TABLE 10. SUMMARY OF CRITERIA POLLUTANTS

Test Date	Sample Location	Emission Factor, ng/J							
		SO_2	NO_x (as NO_2)	CO	Total Particulates*	C_1- C_6 Organics	C_7- C_{16}* Organics	$>C_{16}$ Organics*	Total Organics
8-24	Air heater inlet	1089	325	6.3	NM‡	NM	NM	NM	NM
	Scrubber inlet	2539	247	NM	ND†	0.2 -0.7	ND	ND	ND
	Scrubber outlet	284	293	NM	ND	0.4 -0.9	ND	ND	ND
8-28	Air heater inlet	1912	202	8.4	ND	0.32-0.7	ND	ND	ND
	Scrubber inlet	2750	237	NM	ND	0.42-0.8	ND	ND	ND
	Scrubber outlet	318	231	NM	ND	0.38-0.9	ND	ND	ND
8-29	Air heater inlet	1980	176	14	ND	0.2 -0.5	ND	ND	ND
	Scrubber inlet	2517	256	NM	ND	0.3 -0.7	ND	ND	ND
	Scrubber outlet	271	221	NM	ND	0.6 -1.0	ND	ND	ND
8-30	Air heater inlet	1710	193	35	NM	NM	NM	NM	NM
	Scrubber inlet	2238	345	NM	ND	0.41-0.8	ND	ND	ND
	Scrubber outlet	245	307	NM	ND	1.9 -2.1	ND	ND	ND
9-6	Air heater inlet	1944	NM	NM	NM	NM	NM	NM	NM
	Scrubber inlet	2366	NM	NM	NM	NM	NM	NM	NM
	Scrubber outlet	NM	NM	NM	NM	NM	NM	NM	NM
9-11	Air heater inlet	2206	NM	NM	NM	NM	NM	NM	NM
	Scrubber inlet	NM	NM	NM	NM	NM	NM	NM	NM
	Scrubber outlet	NM	NM	NM	NM	NM	NM	NM	NM
9-12	Air heater inlet	2052	NM	NM	NM	NM	NM	NM	NM
	Scrubber inlet	2474	NM	NM	NM	NM	NM	NM	NM
	Scrubber outlet	214	NM	NM	NM	NM	NM	NM	NM
9-13	Air heater inlet	2054	NM	NM	NM	NM	NM	NM	NM
	Scrubber inlet	2474	NM	NM	NM	NM	NM	NM	NM
	Scrubber outlet	NM	NM	NM	NM	NM	NM	NM	NM
Average	Air heater inlet	1968	224	16	1590	0.2-0.6	0.089	0.33	0.6-1.0
	Scrubber inlet	2402	271	NM	39.8	0.3-0.7	0.019	0.18	0.5-0.9
	Scrubber outlet	266	263	NM	2.65	0.8-1.2	0.012	0.059	0.9-1.3

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*Total particulate and $>C_7$ organics data are composites obtained by continuous SASS operation on test days during the period 8-24 to 8-30. Daily loading data were not obtained.

†ND indicates that data are not available on a daily basis, although composite data were obtained.

‡NM indicates that this parameter was not measured on this day.

TABLE 11. COMPARISON OF UNCONTROLLED CRITERIA POLLUTANT EMISSIONS WITH EPA AP-42 EMISSION FACTORS FOR COAL-FIRED UTILITY BOILERS

Pollutant	Emission Factor, ng/J Air Heater Inlet	Scrubber Inlet	AP-42 Emission Factor
SO_2	1968	2482	2300
NO_x (as NO_2 at 70% load)	224	271	310
CO	16	No Data	20
Total Particulate	1590	39.8*	3700
Total Organics	0.6-1.0	0.5-0.9	5

* Controlled particulate data are not comparable to AP-42 data.

Because SO_2 emission factors are dependent upon flue gas O_2 analyses, in addition to SO_2 analyses, these data were examined in an effort to resolve discrepant results obtained at the air heater inlet. Measured O_2 concentrations were found to correspond well with those estimated from fuel ultimate analyses and measured CO_2 concentrations, indicating that the O_2 analyzer was functioning properly. Daily checks on instrument zero and span (against a 5% O_2 calibration gas) also indicated proper operation of the O_2 analyzer. The SO_2 analyzer was found to drift somewhat during each test day; at the conclusion of each test day, SO_2 measurements were found to be low by up to 10% relative to a 1054 ppm calibration gas, although the average drift for the test period was only 5%. Air leakage into the sample system does not appear to be a problem because leakage into the main sampling line would have offsetting affects on the O_2 and NO_x analyzers, and would not affect emission factors. Leakage in the vicinity of the analyzers (downstream of the gas conditioner) is precluded since the analysis system gas pressure was 7kPa above atmospheric pressure. Hence, based upon available data, apparent discrepancies in the air heater inlet SO_2 data can be partially attributed to instrument drift although complete resolution cannot be achieved.

Average SO_2 emissions measured at the scrubber outlet were 266 ng/J. This corresponds to an average SO_2 removal efficiency of 89% based upon the average scrubber inlet SO_2 level with a slight correction for tail gas addition.

Nitrogen Oxides--

Average NO_x levels measured were 224 ng/J (expressed as NO_2) at the air heater inlet, 271 ng/J at the scrubber inlet, and 263 ng/J at the scrubber outlet. These levels for 70% boiler load appear reasonable with respect to the AP-42 full load emission factor of 310 ng/J. Although NO_x emissions measured at each of the three sampling locations correspond reasonably well based on overall test averages, examination of daily averages indicates good correlation between the scrubber inlet and outlet values while correlation between these values and those measured at the air heater inlet is generally poor. NO_x data measured at the air heater inlet differ from the average of scrubber inlet and outlet NO_x data by 14 to 41% on a daily basis. Differences do not indicate a bias and, based upon available data, cannot be attributed to instrumentation problems (NO_x or O_2 analyzers) or air leakage.

Carbon Monoxide--

Carbon monoxide concentrations were measured only at the air heater inlet. Although air leakage across the air heater may reduce CO levels slightly, neither the ESP nor the scrubber are expected to affect CO levels. Therefore, measured CO data should accurately reflect actual emission levels. Measured CO emission levels ranged from 6.3 to 35 ng/J with a mean emission factor of 16 ng/J. These values correspond well with the AP-42 emission factor of 20 ng/J for bituminous coal-fired utility boilers.

Total Particulates--

Total particulates were determined using the Level 1 (SASS) sampling train. The particulate sample was composited during the four days of Level 1 testing and daily loading data were not obtained. The particulate level measured at the air heater inlet (uncontrolled particulates) was 1590 ng/J which is only 43% of the 3700 ng/J uncontrolled emission factor presented in AP-42. This would indicate that only 37% of the fuel ash was present as entrained particulate rather than the 85% indicated by AP-42 for pulverized coal-fired, dry bottom utility boilers. Examination of the sampling location indicates that this discrepancy is probably the result of particulate stratification in the flue gas duct. Sampling ports are located in the top of a horizontal, rectangular duct which is 1.7 m high, 12.4 m wide, and 4.3 m long. The duct provides a horizontal run connecting the economizer and the air heater inlet, which are both vertically oriented. Thus, the vertically downward flow of flue gas through the economizer and the air heater is interrupted by a short horizontal run attached at right angles to the vertical ducting. The sampling ports are located midway along the length of the horizontal duct, approximately 2.1 m from each right angle bend. Because of the large duct width and the proximity of the sampling ports to the right angle bend at the economizer outlet (which could act as a centrifugal separator), stratification of particulates within the horizontal duct appears probable. It should be noted that this sampling location was selected for use during FGD acceptance and demonstration testing, and during this study because no suitable alternative sampling ports existed in the vicinity of the ESP inlet.

Particulate loadings at the scrubber inlet and outlet were 39.8 and 2.65 ng/J, respectively. These data indicate a scrubber particulate removal efficency of 93%.

Total Organics--

Average data for the test period indicate total organic levels in the range of 0.5 to 1.3 ng/J. Total organic levels at the air heater inlet were o.6-1.0 ng/J and those at the scrubber inlet were 0.5-0.9 ng/J. These levels are less than 20% of the 5 ng/J level presented in AP-42. The C_1-C_6 fraction comprised 33-60% of the total organics at the air heater inlet and 60-78% of the total at the scrubber inlet. Average total organic emissions after scrubbing were 0.9-1.3 ng/J; however, this average emission factor has a slightly high bias resulting from the significantly higher than average C_1-C_6 emissions measured on test day 8-30. The average total organic emissions exclusive of day 8-30 C_1-C_6 results are 0.6-1.0 ng/J which is essentially identical to those measured at the air heater and scrubber inlet. Slight increases in light hydrocarbon concentrations across the scrubber may result from incomplete combustion of fuel in the tail gas incinerator (tail gas is introduced downstream of the scrubber inlet sampling point).

Data for C_7-C_{16} and >C_{16} organic fraction levels indicate successive removal of these fractions across the ESP and the scrubber. The ESP removed 79% of the C_7-C_{16} fraction and 45% of the >C_{16} fraction. Scrubbing further reduced C_7-C_{16} and >C_{16} organic fraction levels by 8% and 37%, respectively. Hence, total removal of the C_7-C_{16} fraction was 87% and that for the >C_{16} fraction was 82%. Emissions of the C_7-C_{16} and >C_{16} fractions to the atmosphere were 0.012 ng/J and 0.059 ng/J, respectively.

4.4.2 Particle Size Distribution

Two methods were employed to obtain particle size distribution data: 1) particle separation by cyclones (via SASS sampling) and 2) inertial impaction using the MRI impactor. SASS train particle size distributions were obtained at the air heater inlet, scrubber inlet, and scrubber outlet while MRI size distributions were obtained at the scrubber inlet and outlet. Size distribution data from SASS and MRI tests are summarized in Tables 12 and 13, respectively.

Data from SASS tests indicate that particulate removal efficiencies of the ESP and the scrubber decrease with decreasing particle size, as would be expected. ESP removal efficiencies for particles larger than 3 μm ranged from 96.0 to 98.6% and decreased to 58.7% for particles smaller than 1 μm. However, as noted previously, particulate collected at the air heater inlet appears to be non-representative as a result of stratification. Since particulate smaller than 3 μm exhibits transport behavior similar to that of a gas, these particles are not readily segregated and measured data for particles in this size range are expected to be accurate. Particles larger than 3 μm are more susceptible to segregation and, therefore, measured data for the 3-10 μm and >10 μm fractions probably indicate erroneously low particulate loadings.

The SASS was operated at the scrubber outlet with only a 3 μm cyclone and a particulate filter because of the low particulate loading in the scrubbed gas. Data presented in Table 12 indicate that particles larger than 3 μm were removed with 99.8% efficiency by scrubbing while those smaller than 3 μm were removed with 82.3% efficiency.

TABLE 12. PARTICLE SIZE DISTRIBUTIONS MEASURED WITH THE SASS[*]

Aerodynamic Diameter Size Range, μ m	Weight %			Emission Factor, ng/J			Removal Efficiency, %	
	Air Heater Inlet	Scrubber Inlet	Scrubber Inlet	Air Heater Inlet	Scrubber Inlet	Scrubber Outlet	ESP	Scrubber
>10	43.9	24.7	No data	698	9.8	No data	98.6	No data
3-10	42.5	38.6	2.3 (>3 μm)†	676	15.4	0.06 (>3 μm)†	97.7	99.8 (>3 μm)†
1-3	12.6	20.1	97.7 (<3 μm)†	200	8.0	2.59 (<3 μm)†	96.0	82.3 (<3 μm)†
<1	1.0	16.6	No data	16	6.6	No data	58.7	No data
Total	100	100	100	1590	39.8	2.65	97.5	93.3

[*] This determination is a Level 1 procedure.

[†] Because of the low particulate loading at the scrubber outlet, only the 3 μm cyclone and the particulate filter were used. Only 2.3% of the scrubber outlet particulate catch was found to be larger than 3 μm.

TABLE 13. PARTICLE SIZE DISTRIBUTIONS MEASURED WITH THE MRI IMPACTOR*

Scrubber Inlet					Scrubber Outlet				
			Particulate Loading					Particulate Loading	
Test Date	Stage	D_{50}, µm	mg/m^3 (7.3% O_2)	$\frac{ng}{J}$	Test Date	Stage	D_{50}, µm	mg/m^3 (7.7% O_2)	$\frac{ng}{J}$
9-11	1	19.72	1.36	0.546	9-11	1	22.87	0.368	0.152
	2	9.646	1.07	0.429		2	11.21	0.368	0.152
	3	3.586	1.22	0.489		3	4.198	0.465	0.192
	4	1.610	1.22	0.489		4	1.909	0.873	0.361
	5	0.9060	1.55	0.622		5	1.093	1.31	0.541
	6	0.4073	1.36	0.546		6	0.5141	1.65	0.682
	7	0.2578	1.36	0.546		7	0.3397	15.7	6.49
	Filter	---	> 2.16†	>0.866†		Filter	---	>25.8†	>10.7†
	Total	---	>11.30	>4.533		Total	---	>46.5	>19.3
9-12	1	22.92	0.996	0.399	9-12	1	22.68	0.369	0.153
	2	11.22	0.865	0.347		2	11.12	0.466	0.193
	3	4.180	3.41	1.37		3	4.160	1.02	0.421
	4	1.884	4.06	1.63		4	1.889	1.84	0.760
	5	1.066	2.49	0.999		5	1.080	2.96	1.22
	6	0.4859	1.26	0.505		6	0.5058	4.37	1.81
	7	0.3116	0.996	0.399		7	0.3328	12.82	5.30
	Filter	---	> 0.43†	>0.172†		Filter	---	> 7.09†	> 2.93†
	Total	---	>14.51	>5.821		Total	---	>30.94	>12.79
9-13	1	26.68	1.01	0.405	9-13	1	22.56	0.364	0.150
	2	13.07	1.14	0.457		2	11.06	0.766	0.317
	3	4.886	3.46	1.39		3	4.137	0.958	0.396
	4	2.215	3.19	1.28		4	1.879	1.25	0.517
	5	1.263	2.00	0.802		5	1.074	2.01	0.831
	6	0.5877	1.86	0.746		6	0.5027	2.68	1.11
	7	0.3842	0.479	0.192		7	0.3306	10.4	4.30
	Filter	---	> 0.57†	>0.229†		Filter	---	> 4.12†	>1.70†
	Total	---	>13.71	>5.50		Total	---	>22.5	>9.32

*Level 2 procedures were utilized.

†Portions of the filter edges were torn as a result of adhering to their mountings. Hence, only lower limit particulate loadings are known. Filters from the scrubber inlet showed no weight gain and tabulated values are based on sulfate analyses. Material lost is estimated not to exceed approximately 10 mg which corresponds to 5.6 ng/J (14 mg/m^3) at the scrubber inlet and 2.1 ng/J (5 mg/m^3) at the scrubber outlet.

Size distribution determinations were performed with MRI impactors on three consecutive days at the scrubber inlet and outlet. MRI tests were performed approximately two weeks after the SASS tests and the boiler load was approximately 84 MW rather than the 80 MW level maintained during SASS testing (refer to Tables 4 and 7). Data from impactor tests are summarized in Table 13. Tabulated D_{50} values are the aerodynamic diameters of particles which will be collected by the specified stage with 50% efficiency. Total particulate loading data and weight percentage data for particles smaller than approximately 0.3-0.4 μm were not obtained because portions of the collection filters adhered to their mountings and were torn from the filters during disassembly. Tabulated lower limit loading values for scrubber inlet filters are based upon sulfate analyses data since no weight gain was measured. Tabulated lower limit values for the scrubber outlet filters are based upon measured weight gains since these exceeded the loadings indicated by sulfate analyses. It should be noted that the average filter weight is 100 mg and that tearing was limited to the filter edges only. Based upon available data, it is estimated that the maximum material loss from the filters as a result of tearing is on the order of 10 mg which corresponds to approximately 5.6 ng/J (14 mg/m^3) at the scrubber inlet and 2.1 ng/J (5 mg/m^3) at the scrubber outlet.

The three sets of impactor data obtained at the scrubber inlet indicate relatively good reproducibility. However, scrubber inlet size distributions and estimated total particulate loadings obtained with the MRI impactor differ substantially from those determined with the SASS. MRI data indicate that the <1 μm fraction comprises at least 19-57% of the total catch (based upon maximum estimated filter losses, this may be as high as 58-78%) while SASS data indicate that approximately 17% of the particulate are smaller than 1 μm. The average maximum estimated total particulate catch obtained with the MRI impactor (10.5 ng/J) is less than 30% of that measured with the SASS (39.8 ng/J). These data indicate that a significant portion of particulates larger than 1 μm which were present during SASS testing either were not present in the flue gas during MRI testing, or were not detected. One possible explanation of the observed discrepancies is that adjustment of the ESP was performed during the down time between Level 1 and Level 2 testing.

However, because conclusive resolution of these discrepancies cannot be achieved with available data, MRI impactor data measured at the scrubber inlet should be considered suspect. Note that the SASS data represent a four day composite with a sample volume 114 m^3 while each of the MRI impactor tests involved sampling less than 1 m^3.

Impactor data obtained at the scrubber outlet also demonstrated reasonable reproducibility as indicated by the differential mass loading data presented in Figure 8. Data spread noted in the figure indicate the uncertainty associated with mass determinations. These data show that more than 76% of the scrubber outlet particulate are less than 1 μm in diameter and are capable of deep lung penetration. Inhalable particulates, those smaller than 15 μm, comprise more than 98% of the scrubber outlet particulate.

The substantial increase in total particulate loading measured at the scrubber outlet with the MRI impactor as compared with SASS data is largely attributable to H_2SO_4 aerosol which is not measured by the SASS. Because flue gas temperatures at the scrubber outlet were approximately 327K with a moisture content of 13%, essentially all of the SO_3 present in the flue gas would be condensed H_2SO_4 (the acid dew point for this system is estimated to be 405K). The SASS cyclones and filter are operated at 477K and would evaporate condensed H_2SO_4 provided the acid has not reacted with ash constituents. Average operating temperatures of the MRI impactors ranged from 384K to 395K to prevent moisture fouling, and condensed acid would not completely evaporate after impaction. Sulfate analyses (presented subsequently) indicate that less acid aerosol was collected with each successive day of MRI testing. This trend is consistent with the average impactor operating temperatures of 384K, 390K and 395K on successive test days; the fraction of H_2SO_4 aerosol collected will tend to decrease with increasing temperature.

4.4.3 Sulfur Compounds: SO_2, SO_3, and $SO_4^=$

Sulfur species were determined by several methods during the test period. The CCS was utilized at the air heater inlet, scrubber inlet, and scrubber outlet to determine SO_2, SO_3, and $SO_4^=$. Particulate sulfate was also determined by extraction of solids collected with the SASS at these three locations and with the MRI impactors at the scrubber inlet and outlet. Additionally, SO_2 was continuously monitored during the test period.

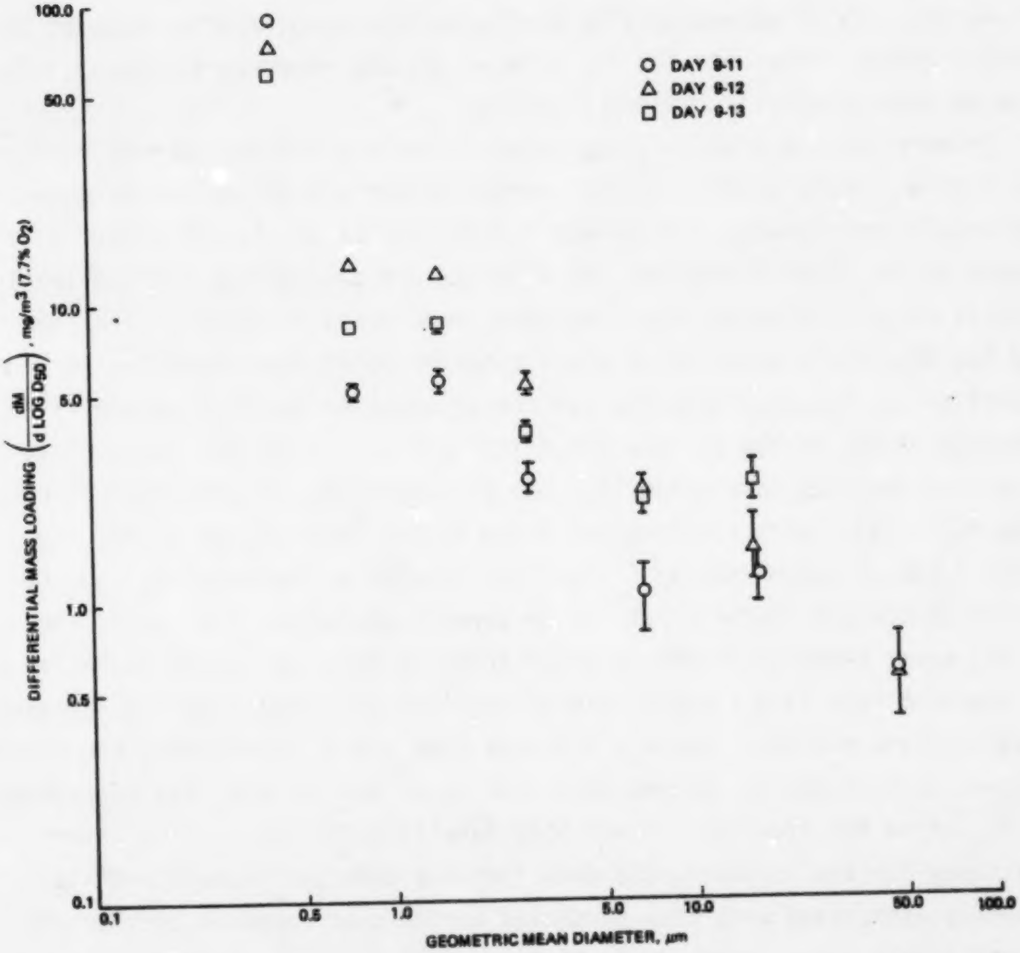

Figure 8. Scrubber Outlet Size Distribution Data Differential Mass Loading

Results of sulfur species determinations by CCS are summarized in Table 14. Average emissions data show that SO_2 comprised approximately 99.4% of the flue gas sulfur species before scrubbing and 96.4% after scrubbing. The average SO_2 removal efficiency was 86%, based upon CCS data from the scrubber inlet and outlet. A somewhat higher removal efficiency, 91%, was indicated by continuous SO_2 monitoring during this period, although only one scrubber outlet data point is available. It should be noted that continuous monitor SO_2 data obtained at the air heater inlet are considered to be low based upon SO_2 generation estimates from fuel sulfur data (Section 4.4.1); those obtained at the scrubber inlet are consistent with fuel sulfur data. Although average CCS SO_2 data are in agreement with available continuous monitor data at the scrubber inlet, individual CCS SO_2 data points are somewhat scattered. The cause of data scatter is presently unknown.

Primary sulfate data (SO_3 expressed as sulfate and particulate sulfates) show little primary sulfate removal across either the ESP or the scrubber. As discussed previously, particulate stratification at the air heater inlet appears to have been a problem. Particulate and particulate sulfate levels measured at this location are, therefore, considered to be low. The relatively low SO_3 levels measured at the air heater inlet are attributed to adsorption and reaction with fly ash constituents on the particulate filter. Retention of SO_3 on the particulate filter has been shown to increase with decreasing sampling rate below 10 l/min and decreasing filter temperature below 533 K (4). With sampling rates and filter temperatures at the air heater inlet of approximately 6 l/min and 470-533 K, respectively, SO_3 retention on the air heater inlet filter appears probable. Similarly, the low SO_3 level measured at the scrubber inlet on day 9-06 is attributed to a low sampling rate (3.3 l/min); this is verified by a corresponding increase in particulate sulfate. Average CCS data from the scrubber inlet and outlet indicate that scrubbing removed less than 3% of the SO_3 and less than 7% of the $SO_4^=$ from the flue gas. Since SASS data show 93% particulate removal efficiency for the scrubber, CCS data indicate that particulate sulfate is primarily associated with fine particles and/or that measured particulate sulfate levels appear erroneously high as a result of SO_3 retention on the filter.

TABLE 14. SO_2, SO_3 AND $SO_4^=$ EMISSIONS DETERMINED WITH THE CONTROLLED CONDENSATION SYSTEM*

Sulfur Compound	Test Date	Emission Factor, ng/J			Mole % of Total Sulfur Species in the Flue Gas		
		Air Heater Inlet	Scrubber Inlet	Scrubber Outlet	Air Heater Inlet	Scrubber Inlet	Scrubber Outlet
SO_2	9-06	2509 (1944)†	No data (2365)†	336	99.4	No data	96.5
	9-11	1672 (2206)†	2938	480	98.9	99.4	97.3
	9-12	2985 (2051)†	2268 (2474)†	293 (214)†	99.5	99.4	94.8
	Average	2389 (2067)†	2603 (2419)†	370 (214)†	99.3	99.4	96.4
SO_3 (Expressed as $SO_4^=$)	9-06	2.62	<1.20	8.05	0.07	No data	1.5
	9-11	6.37	20.6	11.8	0.25	0.47	1.6
	9-12	2.46	12.6	13.9	0.05	0.36	3.0
	Average	3.81	11.5	11.2	0.11	0.29	1.9
$SO_4^=$	9-06	19.6‡	16.8	10.2	0.52‡	No data	2.0
	9-11	21.7‡	7.56	8.38	0.85‡	0.17	1.1
	9-12	21.6‡	6.42	10.1	0.48‡	0.19	2.2
	Average	21.0‡	10.3	9.56	0.58‡	0.26	1.7
Total Primary $SO_4^=$	9-06	22.2‡	18.0	18.2	0.57‡	No data	3.5
	9-11	28.1‡	28.2	20.2	1.10‡	0.64	2.7
	9-12	24.1‡	19.0	24.0	0.53‡	0.55	5.2
	Average	24.8‡	21.7	20.8	0.69‡	0.55	3.6

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*These determinations are Level 2 procedures.

†Parenthetic SO_2 data were obtained simultaneously by continuous pulsed fluorescence analysis at the air heater inlet and by continuous ultraviolet analysis at the scrubber inlet and outlet. Continuous SO_2 monitor data measured at the scrubber inlet are considered to be more accurate than those measured at the air heater inlet based upon fuel sulfur considerations (Section 4.4.1).

‡Available data indicate that particulate stratification was a problem at the air heater inlet. Hence, the validity of particulate sulfate data obtained at this location is questionable.

TABLE 15. PARTICULATE SULFATE EMISSIONS DETERMINED FROM THE SASS PARTICULATE*

Aerodynamic Diameter Size Range, µm	Particulate Sulfate Emissions, ng/J Air Heater Inlet	 Scrubber Inlet	 Scrubber Outlet
>10	6.07[†]	0.344	No data
3-10	11.4[†]	0.436	No data
1-3	4.20[†]	0.305	No data
<1	3.98[†]	1.08	No data
Total	25.6[†]	2.16	0.603

[*] SASS tests were performed during the period 8-24 through 8-30. $SO_4^=$ was determined by Level 2 procedures.

[†] Available data indicate that particulate stratification was a problem at the air heater inlet. Hence, the validity of particulate sulfate data obtained at this location is questionable.

Particulate sulfate data obtined from SASS tests are summarized in Table 15. Sulfate levels were measured at the air heater inlet, scrubber inlet, and scrubber outlet. These data indicate that sulfate removal by the ESP exceeded 92% (sulfate levels measured at the air heater inlet are thought to be low due to particulate segregation). The measured $SO_4^=$ removal efficiency of the scrubber is 72%. Particulate sulfate loadings determined from SASS tests are substantially lower than those indicated by the CCS for the scrubber inlet and outlet. Sulfate loadings indicated by the CCS are a factor of five larger than SASS results for the scrubber inlet and a factor of 16 larger than SASS results for the scrubber outlet. Although SASS tests were performed prior to CCS testing, $SO_4^=$ data from the SASS tests may show that $SO_4^=$ levels indicated by CCS tests are erroneously high as a result of SO_3 retention by the filter.

Particulate sulfate data determined from MRI impactor particulate are summarized in Table 16. Because flue gas temperatures at the scrubber inlet were well above the H_2SO_4 dew point, $SO_4^=$ determined from the impactor plates for this location is particulate sulfate exclusive of condensed SO_3. Flue gas and impactor temperatures at the scrubber outlet were below the H_2SO_4 dew point (approximately 405 K) and, therefore, sulfate on these impactor plates consists of particulate sulfate and H_2SO_4 aerosol. The problem

TABLE 16. PARTICULATE SULFATE EMISSIONS DETERMINED FROM MRI IMPACTOR PARTICULATE*

Scrubber Inlet				Scrubber Outlet			
Test Date	Stage	D_{50}, µm	Emission Factor, ng/J	Test	Stage	D_{50}, µm	Emission Factor, ng/J
9-11	1	19.72	0.052	9-11	1	22.87	0[†]
	2	9.646	0.02		2	11.21	0[†]
	3	3.586	0[†]		3	4.198	0[†]
	4	1.610	0.004		4	1.909	0.058
	5	0.9060	0.076		5	1.093	0.14
	6	0.4073	0.04		6	0.5141	0.15
	7	0.2578	0.02		7	0.3397	3.34
	Filter	---	0.866[‡]		Filter	---	6.82[‡]
	Total	---	1.08		Total	---	10.45
9-12	1	22.92	0.068	9-12	1	22.68	0[†]
	2	11.22	0.22		2	11.12	0[†]
	3	4.180	0.421		3	4.160	0[†]
	4	1.884	0.35		4	1.889	0.03
	5	1.066	0.12		5	1.080	0.058
	6	0.4859	0.048		6	0.5058	0.36
	7	0.3116	0.10		7	0.3328	No Data
	Filter	---	0.17[‡]		Filter	---	1.77[‡]
	Total	---	1.50		Total	---	>2.22
9-13	1	26.68	0.096	9-13	1	22.56	0[†]
	2	13.07	0.044		2	11.06	0[†]
	3	4.886	0.24		3	4.137	0.008
	4	2.215	0.15		4	1.879	0.004
	5	1.263	0.096		5	1.074	0.12
	6	0.5877	0.29		6	0.5027	0.28
	7	0.3842	0.096		7	0.3306	1.87
	Filter	---	0.23[‡]		Filter	---	1.47[‡]
	Total	---	1.24		Total	---	3.75

---

[*] Because of flue gas and impactor temperatures, scrubber inlet sulfate is particulate sulfate exclusive of condensed SO_3, while scrubber outlet sulfates are particulate sulfate and H_2SO_4 aerosol. These data were determined by Level 2 procedures.

[†] Tabulated zero values were actually less than the blank.

[‡] Portions of the filter edges were torn as a result of adhering to their mountings. Hence, only lower limit total particulate loadings are known. Total material lost is estimated not to exceed approximately 10 mg which corresponds to 5.6 ng/J at the scrubber inlet and 2.1 ng/J at the scrubber outlet. Because the filter edges are covered by the mounting during impactor operation, the lost material should be only filter paper and not particulate. For this reason, sulfate loadings determined by extraction are considered accurate and not lower limit values.

with filter tearing, previously discussed in conjunction with size distribution data, is not thought to affect sulfate measurements. Tearing was limited to the filter edges which are covered by their mountings during impactor operation. Hence, any material lost is thought to be paper rather than particulate or aerosol. Sulfate data are determined by extraction and analysis of the extract, not by weighing the filters. Therefore, tabulated sulfate values are considered to be accurate and not lower limit data.

Particulate sulfate determined from impactor tests at the scrubber inlet ranged from 1.08 to 1.50 ng/J. In contrast, $SO_4^{=}$ loadings at the scrubber outlet ranged from 3.75 to 10.45 ng/J (based on available MRI data, the tabulated lower limit value of >2.22 ng/J is expected to be approximately 4 ng/J). The decreasing quantity of H_2SO_4 collected on successive days reflects the increasing average impactor operating temperatures. Average operating temperatures for these three tests were 384 K, 390 K, and 395K, respectively. Scrubber outlet data show that the H_2SO_4 aerosol are fine particulate, generally smaller than 0.5 μm in diameter.

4.4.4 Inorganics

Major and trace elements in the flue gas were primarily determined by inductively coupled plasma optical emission spectroscopy (ICP). Trace elements not determined by ICP are arsenic and antimony which were determined by atomic absorption and mercury which was determined by a cold vapor atomic absorption method. Concentrations of thirty elements present in the flue gas are presented in Tables 17 and 18. To assess the hazard potential of these elemental concentrations, the data are compared with the Discharge Multimedia Environmental Goal (DMEG) values for these elements. The DMEG values are emission level goals developed under the direction of EPA, and can be considered as concentrations of pollutants in undiluted emission streams that will not adversely affect those persons or ecological systems exposed for short periods of time (5). The DMEG values tabulated represent air concentrations which were derived from human health considerations based upon the most hazardous compound formed by the element in question. Additionally, estimated ambient concentrations, based upon measured emission concentrations, are compared with the Ambient Multimedia Environmental Goal (AMEG) values. Tabulated

TABLE 17. FLUE GAS CONCENTRATIONS OF MAJOR AND TRACE ELEMENTS*

Element	Concentration, mg/m^3 Air Heater Inlet ($3.7\%\ O_2$)†	Concentration, mg/m^3 Scrubber Inlet ($9.3\%\ O_2$)	DMEG for Air (Health Basis) mg/m^3	Discharge Severity‡ Air Heater Inlet	Discharge Severity‡ Scrubber Inlet
Al	92.7	1.75	5.2	18	0.34
As	0.565	0.010	0.0020	280	5.0
B	8.00	0.385	3.1	2.6	0.12
Ba	0.737	0.0133-0.0213	0.50	1.5	0.027-0.043
Be	0.028	0.0007-0.001	0.0020	14	0.4-0.5
Ca	166	2.77	16	10	0.17
Cd	0.043-0.045	0.002-0.003	0.010	4.3	0.2-0.3
Co	0.525	0.0657	0.050	10	1.3
Cr	0.476	0.0087	0.0010	480	8.7
Cu	0.142	0.026	0.20	0.71	0.13
Fe	232	4.27	1.0	230	4.3
Ga	0.335-0.350	0.020-0.30	5.0	0.067-0.070	0.0040-0.060
Hg	0.00096	0.00048	0.050	0.019	0.0096
K	1.84-1.89	<0.060	2.0	0.92-0.94	<0.030
La	0.049	0.0016-0.0024	110	<0.001	<0.001
Li	0.184	0.0014	0.022	8.4	0.064-12
Mg	9.38	0.225	6.0	1.6	0.038
Mn	1.03	0.273	5.0	0.21	0.055
Na	3.09-3.14	0.233-0.285	53	0.058-0.059	0.044-0.0054
Ni	0.422	0.0061	0.015	0.28	0.41
P	2.51	0.0406-0.0486	0.10	25	0.41-0.49
Pb	0.528-0.539	0.0141-0.0241	0.15	3.5-3.6	0.094-0.16
Sb	0.030	0.046	0.50	0.060	0.092
Si	0.495	0.407	10	0.049	0.041
Sn	0.440-0.463	<0.04	**	---	---
Sr	0.548-0.564	0.0129-0.0329	3.0	0.18-0.19	0.0043-0.011
Ti	2.17	0.052	6.0	0.36	0.0087
V	0.494	0.0205	0.50	0.98	0.041
Zn	3.90	0.117	4.0	0.97	0.029
Zr	0.0636-0.0641	0.0017-0.0027	5.0	0.013	<0.001

---

* Arsenic and antimony were determined by atomic absorption (Level 2) and mercury was determined by a cold vapor method (Level 1). All other elements were measured by ICP (Level 2).

† Based upon available data, concentrations at the air heater inlet are considered to be low as a result of particulate stratification.

‡ Discharge severity is defined as the ratio of the discharge concentration to the DMEG value. A discharge severity greater than 1.0 is indicative of a potential hazard requiring further characterization.

** A DMEG value has not been established for tin.

TABLE 18. EMISSION CONCENTRATIONS OF MAJOR AND TRACE ELEMENTS*

Element	Concentration, $\mu g/m^3$ (9.15% O_2)	DMEG, $\mu g/m^3$ (Health Basis)	Discharge Severity	AMEG, $\mu g/m^3$ (Health Basis)	Ambient Severity†
Al	464-480	5,200	0.089-0.092	12.6	0.0368-0.038
As	0.80	2.0	0.40	0.0050	0.160
B	80	3,100	0.026	74	0.001
Ba	1.8-20	500	0.0036-0.040	1	0.002-0.02
Be	0.05-0.5	2	0.02-0.2	0.01	0.005-0.05
Ca	42.6-50	16,000	0.0027-0.003	**	---
Cd	0.10-3	10	0.01-0.3	0.02	0.005-0.15
Co	10	50	0.2	0.1	0.1
Cr	0.27	1	0.27	0.002	0.1
Cu	10	200	0.05	0.5	0.02
Fe	47	1,000	0.047	**	---
Ga	0.48-30	5,000	<0.001	9	<0.003
Hg	0.00	50	0.00	0.01	0.00
K	3.2-80	2,000	0.0016-0.040	5	0.001-0.02
La	0.03-2	110,000	<0.001	**	---
Li	<0.1	22	<0.005	0.05	<0.002
Mg	4.8-20	6,000	0.0008-0.003	14	<0.001
Mn	56	5,000	0.011	12	0.0047
Na	165-260	53,000	0.0031-0.0049	**	---
Ni	<0.3	15	<0.02	0.035	<0.009
P	2.9-20	100	0.029-0.2	0.24	0.012-0.083
Pb	<20	150	<0.1	0.36	<0.06
Sb	326	500	0.652	1.2	0.27
Si	<50	10,000	<0.005	**	---
Sn	<50	‡	---	**	---
Sr	<30	3,000	<0.01	5.5	<0.005
Ti	1.9-2.7	6,000	<0.001	14	<0.001
V	1.4-3	500	0.0028-0.006	1.2	0.0012-0.0025
Zn	20	4,000	0.005	9.5	0.002
Zr	<2	5,000	<0.001	**	---

* Arsenic and antimony were determined by atomic absorption (Level 2) and mercury was determined by a cold vapor method (Level 1). All other elements were measured by ICP (Level 2).

† Ambient discharge severity is defined as the ratio of the ambient concentration to the AMEG value. The ambient concentration is estimated to be the ratio of discharge concentration and a dilution factor based upon the flue gas flow rate. At 80 MW, the flow rate is 156 kg/s and the corresponding dilution factor is 1000. An ambient severity greater than 1.0 is indicative of a potential hazard requiring further characterization.

‡ A DMEG value has not been established for tin.

** AMEG values have not been established for these elements.

AMEG values are analogous to DMEG values with the exception that AMEG concentrations will not adversely affect persons or ecological systems subjected to continuous exposure.

Elemental concentrations were determined by analyzing the SASS catches obtained during the test period. As will be discussed in the Appendices, major and trace elements are recovered from the particulate catches by aqua regia extraction. Because some particulate constituents are insoluble in aqua regia (i.e., silica and some aluminosilicates), tabulated elemental concentrations do not necessarily reflect the total elemental concentration in the flue gas. However, the rigorous extraction procedure employed ensures that tabulated elemental concentrations are equal to or greater than concentrations available to the environment as a result of natural extraction processes.

Elemental data presented in Table 17 indicate that at least 14 elements exceeded their respective DMEG values at the air heater inlet (Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Fe, Li, Mg, Pb, and P). Because the SASS particulate catch at the air heater inlet appears to have been low as a result of particulate stratification, other elements may also have exceeded their DMEG values at this location. Scrubber inlet data indicate that, after particulate removal by the ESP, only four elements exceeded their respective DMEG values. These four elements, arsenic, cobalt, chromium, and iron, would be of concern in the absence of further flue gas treatment. The DMEG value for arsenic is low because arsenic is a cumulative poison producing chronic effects in humans. Cobalt is also a cumulative poison, and may produce liver and kidney damage as well as some pulmonary effects, allergic-type dermatitis and digestive changes. Chromium has a low DMEG value due to considerations of potential human carcinogenicity.

Scrubber outlet data presented in Table 18 indicate that flue gas elemental concentrations after scrubbing do not pose a health hazard with either short term direct exposure or continuous exposure after dispersion. However, it should be noted that neither DMEG nor AMEG values have been established for tin, and AMEG values have not been established for calcium, iron, lanthanum, sodium, silicon, and zirconium.

Major and trace element emission factors are presented in Table 19 with estimated removal efficiencies for the ESP and scrubber units. The overall elemental removal efficiency of the ESP was measured to be 97%; however, the actual removal efficiency may have been higher since concentrations at the air heater inlet are probably lower limit values due to the apparent particulate stratification at this location. The overall elemental removal efficiency of the scrubber was 85 to 89%, resulting in an average combined removal efficiency exceeding 99.5%.

Parallel with these elemental and anion analyses, X-Ray Diffraction (XRD) and Fourier Transform Infrared (FTIR) spectroscopic analyses for individual compounds were conducted. Detailed FTIR results and spectra are presented in Appendix D and summarized in Table 20 with the XRD results. The FTIR results clearly showed that materials like $CaSO_4$, Fe_3O_4, and $NaHSO_4$ tended to be found in the smaller (<1 μm) particle sizes. There is evidence to show that $NaHSO_3$ was emitted from the FGD since $NaHSO_4$, an oxidative product of $NaHSO_3$, was found in the FGD outlet samples but not in the inlet filter samples. In terms of absolute emissions, however, the $NaHSO_3$ emission appears to be less than 0.5 ng/J, based on Na emission data.

Flue gas nitrate data were obtained by extraction of SASS catches and are summarized in Table 21. Separate nitrate determinations were made for the >3 μm particulate fractions and the <3 μm particulate fractions. These data indicate nitrate levels of 0.215 to 0.219 ng/J at the air heater inlet, 0.003 to 0.006 ng/J at the scrubber inlet and 0.004 at the scrubber outlet.

Specific anion analyses were also preformed on the extracts from particulate catches and impinger solutions from the CCS. Chloride and fluoride analyses are summarized in Table 22. Emissions of particulate chloride and HCl were 0.09 and 0.25 ng/J, respectively. Chloride concentrations at the air heater inlet and scrubber inlet exceeded the DMEG value (7000 $\mu g/m^3$) but the discharge severity at the scrubber outlet was only 0.11. Owing to the low levels of particulate chloride, removal efficiencies achieved during two tests cannot be determined; however, tests conducted on 9-12 indicate that at least 63% removal was achieved overall. The removal efficiency of the ESP cannot be reliably computed since particulate catches at the air heater inlet appear to be low as a result of particulate stratification. HCl was not removed by the ESP although scrubbing affected 91% removal, or more.

TABLE 19. EMISSION FACTORS FOR MAJOR AND TRACE ELEMENTS[*]

Element	Emission Factor, pg/J			Removal Efficiency, %		
	Air Heater Inlet[†]	Scrubber Inlet	Scrubber Outlet	ESP[†]	Scrubber	Total[†]
Al	29,400	822	215-223	97	73-74	99.2
As	179	4.7	0.37	97	92	99.8
B	2,540	181	37	93	80	99
Ba	234	6.23-10.0	0.83-0.90	96-97	86-92	99.6
Be	89	0.3-0.5	0.02-0.2	99.9	33-96	99.8-99.9
Ca	52,700	1,300	19.8-23	98	98	99.9
Cd	14	0.9-1	0.046-1	93	≤95	93-99.7
Co	167	30.9	5	81	84	97
Cr	151	4.1	0.13	97	97	99.9
Cu	45.1	12	4.6	73	62	90
Fe	73,700	2,010	22	97	99	99.9
Ga	106-111	9.4-140	0.22-14	≤91	≤99.8	87-99.8
Hg	0.30	0.23	0.00	23	100	100
K	585-600	28	1.5-37	>95	<95	94-99.7
La	16	0.75-1.1	0.01-0.9	93-95	≤99	94-99.9
Li	58.5	0.66	<0.05	99	>92	>99.9
Mg	2,980	106	2.2-9.3	96	91-98	99.7-99.9
Mn	372	128	26	66	80	93
Na	982-997	109-134	76.5-121	86-89	<43	88-92
Ni	134	2.9	<0.1	98	>97	>99.9
P	797	19.1-22.8	1.3-9.3	97-98	51-94	99-99.8
Pb	168-171	6.62-11.3	<9.3	93-96	Unknown	94-95
Sb	9.6	21.4	151	<0	<0	<0
Si	157	191	<23	<0	>88	>85
Sn	140-147	<20	<23	>85	Unknown	>84
Sr	174-179	6.06-15.5	<14	91-97	Unknown	>92
Ti	689	24	0.88-1.3	97	95-96	99.8-99.9
V	157	9.63	0.65-1	94	90-93	99.4-99.6
Zn	1,240	55.0	9.3	96	83	99.2
Zr	20.2-204	0.80-1.3	<0.9	≥94	Unknown	>95.5
Total	168,000-168,200	5,060-5,290	574-768	97	85-89	99.5-99.7

[*] Arsenic and antimony were determined by atomic absorption (Level 2) and mercury was determined by a cold vapor method (Level 1). All other elements were measured by ICP (Level 2).

[†] Based upon available data, elemental concentrations at the air heater inlet are considered to be low as a result of particulate stratification. ESP and total removal efficiencies estimated from these data are probably low.

TABLE 20. SUMMARY OF FTIR AND XRD ANALYSIS OF NIPSCO FLUE GAS PARTICULATE SAMPLES

Sample	Sample Type and Location	Species Found by FTIR	Species Found by XRD
164-CC	Combined 10μm and 3μm cyclone catch at the air heater inlet	SiO_2 "Silicate matrix" $CaSO_4$ Fe_3O_4	$LiAlSiO_2$ $Ca(Al_2Si_2O_8)\cdot 4H_2O$ SiO_2 $AlPO_4$
164-1C	1 μm cyclone catch at the air heater inlet	SiO_2 "Silicate matrix" Fe_3O_4 $CaSO_4$	$LiAlSiO_2$
164-PF	Filter catch at the air heater inlet	$CaSO_4$ Fe_3O_4 "Silicate matrix" SiO_2	(Spectra too weak)
165-CC	Combined 10μm and 3μm cyclone catch at the scrubber inlet	SiO_2 "Silicate matrix" Fe_3O_4	$LiAlSiO_2$ $Ca(Al_2Si_2O_8)\cdot 4H_2O$ Fe_3O_4
165-1C	1 μm cyclone catch at the scrubber inlet	SiO_2 "Silicate matrix" Fe_3O_4 $CaSO_4$ $NaHSO_4$ $ZnSO_4$	$LiAlSiO_2$
165-PF	Filter catch at the scrubber inlet	"Silicate matrix" $CaSO_4$ $NaHSO_4$ (Unknown sulfate)	$CaSO_4\cdot 2H_2O$ (Na_2SO_4 - possibly)
166-PF	Filter catch at the scrubber outlet	$CaSO_4$ $NaHSO_4$ "Silicate matrix"	$CaSO_4$ (Na_2SO_4 - possibly)

Emissions of particulate fluoride and HF were 0.004 and 0.3 ng/J, respectively. Fluoride concentrations at the air heater inlet and scrubber inlet exceeded the DMEG value (2500 $\mu g/m^3$) but the discharge severity at the scrubber outlet was only 0.029. Scrubbing removed at least 60% of the particulate fluoride and the overall removal exceeded 87%. Little or no HF was removed by the ESP, although scrubbing effected approximately 97% removal.

These data indicate that neither Cl^- or F^- emissions appear to pose a health hazard with short term direct exposure. AMEG values have not been established for these anions, so the potential hazards of long term exposure after dispersion cannot be evaluated.

TABLE 21. FLUE GAS NITRATE EMISSION FACTORS*

Aerodynamic Diameter Size Range, μm	Emission Factor, ng/J		
	Air Heater Inlet	Scrubber Inlet	Scrubber Outlet
>3	0.215	<0.003	No data†
<3	<0.0038	0.003	0.004
Total	0.215-0.219	0.003-0.006	0.004

[*] Level 2 procedures were utilized.

[†] An inadequate quantity of material was available for nitrate analysis. The total >3 μm catch was 0.0074 ng/J. Based on the 0.01% nitrate concentration determined for the other >3 μm particulate catches, this fraction would have a nitrate emission factor on the order of 1 x 10^{-6} ng/J.

4.4.5 Specific Organic Compounds

Flue gas samples from the air heater inlet, scrubber inlet, and scrubber outlet were analyzed for organics using Level 1 procedures. Organics in the C_1-C_6 range were measured using gas chromatographic (GC) analysis of bag samples. SASS samples were analyzed by gas chromatography to determine C_7-C_{16} organics and by gravimetric analysis to determine higher molecular weight organics (>C_{16}). Infrared analyses (IR) were performed on SASS samples to identify specific compound classes, and gas chromatograph/mass spectrometry (GC/MS) analysis was used to quantify POMs.

Results of GC analyses for C_1-C_6 organics are presented in Table 23. In general, the majority of C_1-C_6 organics were present in the C_1 and C_2 fractions with other fractions present at concentrations below the analytical detection limit. A notable exception is the high C_6 organic level (1 ng/J) measured at the scrubber outlet on day 8-30; this single measurement may indicate an upset in the tail gas incineration unit but does not appear to be representative of flue gas emissions from the system. Typical levels of C_1-C_6 organics appear to range from 0.2 ng/J to approximately 1 ng/J.

Chromatographic and gravimetric analyses of the SASS catches are summarized in Table 24. Most C_7-C_{16} organics measured at the air heater inlet

TABLE 22. CHLORIDE AND FLUORIDE EMISSIONS DETERMINED WITH THE CONTROLLED CONDENSATION SYSTEM*

Compound	Test Date	Emission Factor, ng/J			Removal Efficiency, %	
		Air Heater Inlet†	Scrubber Inlet	Scrubber Outlet	Scrubber	Total
Particulate Cl^-	9-06	0.09	0.92	<0.09	Unknown	Unknown
	9-11	0.09	<0.1	<0.09	Unknown	Unknown
	9-12	0.24‡	<0.08	<0.09	Unknown	>63
HCl	9-06	2.7	>3.8	0.25	>93	91
	9-11	3.8	5.10	No data	No data	No data
	9-12	3.3	3.4	0.26	92	92
Particulate F^-	9-06	0.04	0.03	0.002	93	≥95
	9-11	0.03	0.01	<0.004	>60	>87
	9-12	0.03‡	0.001	<0.004	Unknown	>87
HF	9-06	1.1	0.96	0.02	98	98
	9-11	1.1	1.6	0.04	97	96
	9-12	1.7	0.93	0.03	97	98

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*These determinations are Level 2 procedures.

†Particulate chloride and fluoride data at the air heater inlet are questionable as a result of possible particulate stratification at this location.

‡Thirty two percent of the particulate chloride and 27% of the particulate fluoride were obtained with a water rinse of the probe subsequent to the acetone-methylene chloride probe rinse. Hence, acetone-methylene chloride probe rinses appear to be inadequate for complete recovery of particulate from the probe. However, due to the lack of statistically significant data, no correction has been applied to particulate catches recovered without a water rinse.

TABLE 23. C_1-C_6 ORGANICS IN FLUE GAS STREAM *

Emission	Date	Emission Factor, ng/J						
		C_1	C_2	C_3	C_4	C_5	C_6	Total
Air heater inlet	8-28	0.28	0.04	<0.06	<0.08	<0.1	<0.1	0.32-0.7
	8-29	0.1	0.08	<0.06	<0.07	<0.09	<0.1	0.2 -0.5
Scrubber inlet	8-24	0.2	0.05	<0.08	<0.1	<0.1	<0.2	0.2 -0.7
	8-28	0.37	0.05	<0.07	<0.1	<0.1	<0.1	0.42-0.8
	8-29	0.2	0.1	<0.07	<0.1	<0.1	<0.1	0.3 -0.7
	8-20	0.41	<0.05	<0.07	<0.09	<0.1	<0.1	0.41-0.8
Scrubber outlet	8-24	0.33	0.1	<0.08	<0.1	<0.1	<0.2	0.4 -0.9
	8-28	0.33	0.05	<0.08	<0.1	<0.1	<0.2	0.38-0.9
	8-29	0.53	0.1	<0.07	<0.1	<0.1	<0.1	0.6 -1.0
	8-30	0.2	0.1	0.6	<0.1	<0.1	1	1.9 -2.1

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* Determined by gas chromatography (Level 1). The nominal detection limit is 0.1 ppmv which at 8% O_2 in the flue gas corresponds to 1.8×10^{-15} kmol/J.

TABLE 24. ORGANICS GREATER THAN C_6 IN FLUE GAS STREAM [*]

Organic	Emission Factor, ng/J		
	Air Heater Inlet	Scrubber Inlet	Scrubber Outlet
C_7	<0.0003	<0.0005	<0.0005
C_8	0.08	0.012	<0.0005
C_9	<0.0003	<0.0005	0.005
C_{10}	0.0003	0.001	0.0005
C_{11}	0.006	0.004	0.005
C_{12}	0.0003	<0.0005	0.001
C_{13}	0.0003	<0.0005	0.0005
C_{14}	<0.0003	<0.0005	<0.0005
C_{15}	0.0003	0.001	0.001
C_{16}	0.001	0.001	<0.0005
Total TCO	0.089	0.019	0.012
Total Grav ($>C_{16}$)	0.33	0.18	0.059
TCO + Grav	0.42[†]	0.20	0.071

[*] The total chromatographable organics (TCO), C_7-C_{16}, were determined by gas chromatography (Level 1). The TCO detection limit is approximately 0.0001 ng/J at the air heater inlet and 0.0002 ng/J at the scrubber inlet and outlet. The $>C_{16}$ fraction was determined by gravimetric analysis (Level 1). The grav detection limit is approximately 0.01 ng/J at the air heater inlet and 0.02 ng/J at the scrubber inlet and outlet.

[†] The TCO + grav exceeded 0.5 mg/m^3, indicating the need to perform an LC separation.

and scrubber inlet were present in the C_8 fraction. Other fractions were present at concentrations which were orders of magnitude lower or were below the analytical detection limits. At the scrubber outlet, the highest concentrations of C_7-C_{16} organics were present in the C_9, C_{11}, C_{12}, and C_{15} fractions. Total chromatographable organics (TCO) were detected at 0.089, 0.019, and 0.012 ng/J at the air heater inlet, scrubber inlet, and scrubber outlet, respectively. These data indicate a TCO removal efficiency of 79% for the ESP and 37% for the scrubber.

Higher molecular weight organics ($>C_{16}$) were detected at 0.33, 0.18, and 0.059 ng/J at the air heater inlet, scrubber inlet, and scrubber outlet, respectively. The $>C_{16}$ organics data indicate an ESP removal efficiency of 45% and a scrubber removal efficiency of 67%.

Because the concentration of combined C_7-C_{16} and $>C_{16}$ organics measured at the air heater inlet exceeded 0.5 mg/m^3, the SASS sample was fractionated by a liquid chromatographic (LC) separation. LC separation results are presented in Table 25. The TCO material resided primarily in the LC-3 and LC-4 fractions. Compounds which may be associated with these fractions include aromatic, halogenated aromatic and nitro aromatic hydrocarbons, fused hydrocarbons, ethers, epoxides, aldehydes, heterocyclic oxygen compounds, and nitriles. The $>C_{16}$ organics resided primarily in LC-6 which may be associated with compounds such as alcohols, phenols, esters, ketones, amines, heterocyclic nitrogen compounds and alkyl sulfur compounds. IR analyses of the SASS samples are detailed in Appendix C. These analyses indicate the presence of aromatic hydrocarbons, unsaturated hydrocarbons, and esters or phenols.

GC/MS analysis detected no POM in the scrubber inlet and outlet samples at a detection limit of approximately 0.3 µg/m^3. At the air heater inlet, phenanthrene was detected at 0.7 µg/m^3, and fluoranthene and dibenzanthracene were both detected at concentrations below 0.6 µg/m^3. Based on DMEG values, the measured concentrations of these compounds do not appear to pose a hazard with the possible exception of dibenzanthracene; the health-based DMEG value for dibenz(a,h)anthracene is 0.093 µg/m^3.

TABLE 25. LC ANALYSIS OF FLUE GAS AT THE AIR HEATER INLET
(SAMPLE: 164-XMCD-SE-KD)

	TCO mg	GRAV mg	TCO+GRAV mg	Concentration mg/m^3
Total Sample*	8.64	29.02	37.66	1.22
Taken for LC†	6.40	21.51	27.91	0.90
Recovered‡	3.96	13.46	17.42	0.56

	TCO in mg				GRAV in mg					
Fraction	Found in Fraction	Blank	Corrected	Total**	Found in Fraction	Blank	Corrected	Total**	TCO + GRAV Total mg	Concentration mg/DSCM
1	0.11	0.31	0.00	0.00	1.04	0.21	0.83	1.12	1.12	0.036
2	0.22	0.02	0.20	0.27	0.55	0.07	0.48	0.65	0.92	0.030
3	1.77	0.01	1.76	2.37	0.71	0.26	0.45	0.61	2.98	0.096
4	1.26	0.08	1.18	1.59	0.59	0.32	0.27	0.36	1.95	0.063
5	0.33	0.02	0.31	0.42	0.46	0.11	0.35	0.47	0.89	0.029
6	0.57	0.07	0.50	0.67	12.71	3.27	9.44	12.73	13.40	0.433
7	0.01	0.00	0.01	0.01	2.65	1.01	1.64	2.21	3.22	0.072
	4.27	0.51	3.96	5.33	18.71	5.25	13.46	18.15	23.48	0.759

* Quantity in entire sample, determined before LC

† Portion of whole sample used for LC, actual mg

‡ Quantity recovered from LC column, actual mg

**Total mg computed back to total sample

4.5 LIQUID WASTES AND PROCESS LIQUIDS

Six liquid streams were sampled in the field. These included the Lake Michigan and city water supplies, discharge water from the prescrubber, two process streams (thiosulfate purge and the melt tank liquor), as well as the clarifier overflow, which was the final discharge point from the plant. All of these streams were analyzed in the field for standard water quality parameters: pH, alkalinity, hardness, nutrient level, etc. All six of these streams were also analyzed in the laboratory for inorganics using Level 2 methodology. Additional laboratory analyses were performed on four of these streams to determine organics. The two process streams were excluded from organic analysis because measurable quantities of organics were not expected to be found in these streams and because these streams are not normally waste streams. Wherever possible, the results of an analysis have been compared to those levels thought to be safe, or typical for natural waters.

4.5.1 Water Quality Parameters

Characteristics of the six liquid streams sampled are summarized in Table 26. Although lake water was ordinarily used for all input water requirements, city water was also sampled because it may sometimes be used as an alternative supply. The thiosulfate purge, prescrubber slurry, and melt tank liquor were all discharged into the ash pond during the test period. Ash pond overflow is processed through a clarifying pond and subsequently discharged into Lake Michigan. All analyses were performed in the field, except for one set of $SO_4^=$ data which was obtained in the laboratory.

The water parameters for the Lake Michigan sample seem typical compared to most natural, fresh waters. However, the total phosphorus level is somewhat higher than expected for a body of water as large and unproductive as Lake Michigan. This could be indicative of some domestic or industrial pollution sources. Reference to Table 26 shows the city and lake waters to be very similar, indicating that the city water may have originally been drawn from Lake Michigan. The discharge flow into the lake has a somewhat higher pH, and contains considerably more charged ions than the original lake water. Among these are Ca^{++} and Mg^{++}, as indicated by the increased hardness of the effluent.

TABLE 26. WATER QUALITY PARAMETERS[*]

Liquid Stream	pH	Conductivity umhos/cm	Density, Mg/m³	Total Solids, g/m³	Hardness (as $CaCO_3$) g/m³	Alkalinity (as $CaCO_3$) g/m³	Acidity (Methyl Orange) g/m³	Ammonia Nitrogen g/m³	Total Phosphate g/m³	$SO_3^=$ g/m³	$SO_4^=$ g/m³	Combined $SO_3^=$ and $SO_4^=$ (as $SO_4^=$)[††] g/m³
Lake Water	8.31 ± 0.116[†]	225	No data	No data	150	70	0	0	0.1	No data[**]	No data[**]	14
City Water	7.30 ± 0.104[†]	250	No data	No data	190	70	0	0	0.1	22	24	25
Clarifier Overflow	9.57 ± 0.197[†]	410	No data	No data	250	90	0	2.0	0.05	100	120	123
Thiosulfate Purge	5.61 ± 0.071[†]	20,000	No data	No data	>5,000	375	<0.5	0.05	90	No data	>1,000	495,000
Prescrubber Slurry Liquids	2.60 ± 0.571[†]	7,000	0.994 ± 0.002[†]	0.476[‡] ± 0.443[†]	>5,000	0	350	113	2.2	No data	>1,000	2,430
Melt Tank Liquor	6.13 ± 0.028[†]	>20,000	1.32 ± 0.007[†]	No solids in sample	2,000	100	No data	0.05	15.0	No data	>1,000	104,500

[*] Level 1 procedures were utilized.

[†] Indicated ranges represent one standard deviation.

[‡] The individual values were 1.25, 0.171 and 0.335 (replicates), 0.395 and 0.219 (replicates), for three different days.

[**] It is suspected that mislabelling occurred on the aliquot for this analysis. The values obtained in the field were 2,500 g/m³ for SO_3 and 2,750 g/m³ for SO_4. These seem high for lake water, and are believed to represent an analysis on the prescrubber slurry.

[††] This is a laboratory measurement. All others were performed in the field.

All of the process streams had high conductivities. This would be expected of the thiousulfate purge and melt tank effluent because of their high dissolved salt levels. Although the prescrubber is primarily intended to remove particulate, it also absorbs some of the flue gas constituents; this is evidenced by a low pH, high conductivity, and high acidity, as well as other factors. The large standard deviation for the total solids in this stream could indicate large variations in particulate removal efficiency. However, since one sample was particularly atypical (see footnote in Table 26), it is also possible that the equipment was not functioning properly or that make-up water feed rates were higher than normal on this day. The thiosulfate purge and melt tank effluent appear to have similar characteristics, except that the thiosulfate purge contained dense solid matter whereas the melt tank effluent contained no solids at all. This occurred because the melt tank effluent was bled off downstream of the spent reagent filter, whereas the thiosulfate purge was taken past the evaporation-crystallization stage. Therefore, the solid matter in the thiosulfate purge would be sodium sulfite crystals; available data (discussed in Section 4.6.1) indicate that this was the case.

4.5.2 Inorganics

Inorganic analysis results for the liquid streams are presented in Table 27. In addition, the appropriate health and ecological DMEG values are tabulated. Although the thiosulfate purge and melt tank liquor would be combined and dried to produce a dry by-product during normal plant operation, their discharge severities are included here because they were discharged directly into the ash pond during the entire test period. The prescrubber slurry is discharged to the ash pond by design. Supernatant water from the ash pond flows to the clarifier, and the clarifier overflow is discharged directly to the outside environment (i.e., Lake Michigan).

The clarifier overflow does not exceed the acceptable health-based DMEG levels, but does exceed some ecology-based levels. However, a number of those species exceeding ecological DMEG concentrations are present at similar concentrations in the input water supply as well. These include calcium, cadmium, nickel, and lead. Elements which exceed ecological DMEG values and are present at substantially lower levels in the feed water are aluminum, iron and phosphorus. Two reagent purge streams, the thiosulfate purge and

TABLE 27. MAJOR AND TRACE ELEMENT CONCENTRATIONS IN LIQUID STREAMS*

Element	DMEG, mg/l		Lake Water			City Water			Clarifier Overflow		
	Health	Ecology	g/m^3	Discharge Severity		g/m^3	Discharge Severity		g/m^3	Discharge Severity	
				Health	Ecology		Health	Ecology		Health	Ecology
Al	80	1.0	<0.03	<0.001	<0.03	0.008	0.001	0.08	2.02	0.025	2.02
As	0.25	0.05	<0.02	<0.08	<0.4	<0.02	<0.08	<0.4	0.04	0.16	0.8
B	47	25	0.311	0.007	0.01	<0.005	<0.001	<0.001	12.9	0.274	0.516
Ba	5.0	2.5	<0.03	<0.01	<0.01	<0.03	<0.006	<0.012	0.11	0.022	0.044
Ca	240	16	38.8	0.16	2.42	35.7	0.15	2.23	87.4	0.364	5.46
Cd	0.050	0.001	<0.007	<0.14	<7.0	<0.007	<0.14	<7	<0.007	<0.14	<7
Co	0.75	0.25	<0.009	<0.01	<0.04	0.015	0.02	0.06	<0.009	<0.012	<0.036
Cr	0.25	0.25	<0.01	<0.04	<0.04	<0.01	<0.04	<0.04	0.02	0.08	0.08
Cu	5.0	0.050	<0.002	<0.001	<0.04	0.013	0.003	0.26	<0.002	<0.001	<0.04
Fe	1.5	0.25	0.031	0.021	0.124	0.147	0.098	0.588	0.255	0.170	1.02
Hg	0.01	0.25	<0.0001	<0.01	<0.	<0.0001	<0.01	<0.001	<0.0001	<0.01	<0.001
K	30	23	1.4	0.047	0.061	1.1	0.037	0.048	4.4	0.147	0.191
La	1,700	†	<0.003	<0.001	---	<0.003	<0.001	---	<0.003	<0.001	---
Li	0.33	0.38	<0.1	<0.30	<0.26	<0.1	<0.30	<0.26	0.2	0.606	0.526
Mg	90	87	10.8	0.12	0.12	9.8	0.109	0.113	10.3	0.114	0.118
Mn	0.25	0.10	<0.001	<0.004	<0.01	<0.001	<0.004	<0.01	<0.001	<0.004	<0.01
Na	800	†	5.1	0.006	---	3.8	0.005	---	65.8	0.082	---
Ni	0.23	0.010	<0.04	<0.17	<4	<0.04	<0.174	<4	<0.04	<0.174	<4
P	15	0.0005	<0.03	<0.002	<60	<0.03	<0.002	<60	0.26	0.017	520
Pb	0.25	0.05	<0.05	<0.20	<1	<0.05	<0.2	<1	<0.05	<0.20	<1
Sb	7.5	0.2	<0.01	<0.001	<0.05	<0.01	<0.001	<0.05	<0.01	<0.001	<0.05
Si	150	†	0.156	0.001	---	0.59	0.004	---	2.73	0.018	---
Sr	46	†	0.278	0.006	---	0.36	0.008	---	0.606	0.013	---
V	2.5	0.15	<0.003	<0.001	<0.02	0.010	0.004	0.067	0.067	0.027	0.447
Zn	25	0.10	<0.007	<0.001	<0.07	0.303	0.012	3.03	<0.007	<0.001	<0.07

(Continued)

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* Arsenic (As) and antimony (Sb) were determined by atomic absorption (Level 2), and mercury was determined by a cold vapor method (Level 1). All other elements were measured by ICP (Level 2).

† Ecology-based DMEG values have not been established.

TABLE 27. (Continued)

Element	Thiosulfate Purge			Melt Tank Purge			Prescrubber Slurry Liquid		
	g/m^3	Discharge Severity		g/m^3	Discharge Severity		g/m^3	Discharge Severity	
		Health	Ecology		Health	Ecology		Health	Ecology
Al	<3.0	<0.038	<3	<3.0	<0.04	<3	22.2	0.278	22.2
As	1.42	5.7	28.4	No data†	---	---	0.19	0.76	3.8
B	1,560	33.2	62.4		0.30	0.56	215	4.57	8.6
Ba	<3.0	<0.60	<1.2	<3.0	<0.60	<1.20	<0.03	<0.01	<0.01
Ca	9.42	0.039	0.589	4.95	0.02	0.31	89.1	0.37	5.57
Cd	<0.7	<14	<700	0.7	<14	<700	0.018	0.36	18
Co	<0.9	<1.2	<3.6	<0.9	<1.2	<3.6	0.039	0.05	0.16
Cr	<1.0	<4	<4	<1.0	<4	<4	0.32	1.28	1.28
Cu	<0.2	<0.04	<4	<0.2	<0.04	<4	0.045	0.01	0.90
Fe	<0.3	<0.20	<1.2	15.8	10.5	63.2	20.0	13.3	80
Hg	<0.002	<0.2	<0.01	0.0006	0.06	0.0024	0.0022	0.22	0.01
K	180	6	7.8	8.6	0.29	0.37	11.7	0.39	0.51
La	<0.3	<0.001	---	<0.3	<0.001	---	<0.003	<0.001	---
Li	0.4	1.21	1.05	1.0	3.03	2.63	0.1	0.30	0.26
Mg	<4.0	<0.044	<0.046	<4.0	<0.04	<0.05	21.7	0.24	0.25
Mn	<0.1	<0.40	<1.00	<0.1	<0.40	<1	0.178	0.71	1.78
Na	142,000	178	---	77,500	97	---	724	0.91	---
Ni	<4	<17.4	<400	<4	<17.4	<400	0.208	0.90	20.8
P	23.2	1.55	46,400	<3.26	<0.22	<6,520	0.62	0.04	1,240
Pb	<5	<20	<100	<5	<20	<100	0.18	0.72	3.6
Sb	1.42	0.19	7.1	1.76	0.23	8.8	<0.01	<0.001	<0.05
Si	51	0.340	---	<1	<0.01	---	36.6	0.24	---
Sr	<7	<0.152	---	<7	<0.15	---	0.464	0.01	---
V	<0.3	<0.120	<2.0	<0.3	<0.12	<2	0.206	0.08	1.37
Zn	<0.7	<0.028	<7	<0.7	<0.03	<7	0.976	0.04	9.76

† This data point unavailable due to unresolved matrix interference.

the melt tank liquor, exceed or potentially exceed the DMEG values of numerous elements. Especially high discharge severities were indicated for boron (thio purge only), cadmium, iron (melt tank liquor only), lead, nickel, sodium, and phosphorus. Elemental concentrations in the prescrubber slurry liquids exceeded health-based DMEG values for boron, chromium, and iron although ecology-based DMEG values were exceeded for numerous elements. The highest ecology-based discharge severities were indicated for aluminum, cadmium, iron, nickel, and phosphorous.

4.5.3 Organics

Concentrations of C_7 to C_{16} organics and high molecular weight ($>C_{16}$) organics measured in the liquid streams are summarized in Table 28. The high molecular weight fraction can be seen to comprise most of the organic content. Concentrations of the C_7 to C_{16} organics were above detection limits in only four instances, three of which occurred in the lake water sample. Total organic concentrations ranged from 0.361 g/m^3 for the prescrubber slurry stream to 0.083 g/m^3 for the city water supply. No POM was detected in any of the streams with an analytical detection limit of 1.0 mg/m^3. However, this analysis does not preclude the presence of certain compounds such as benzo(a)pyrene (health-based DMEG = 0.3 mg/m^3), which has a health effect DMEG value below the detection limit.

4.6 SOLID WASTES AND PROCESS SOLIDS

Solid or slurry streams sampled during the test period included the feed coal, fly ash, prescrubber slurry, ash pond sludge, thiosulfate purge, soda ash and product sulfur streams. In addition, the melt tank purge, which was free of solids during field analyses, was found to contain a substantial quantity of crystalline solids upon arrival at the laboratory. Three of these streams are waste streams by design: 1) the fly ash, 2) the prescrubber slurry, and 3) the ash pond sludge (which contains fly ash, bottom ash, and any other solid wastes produced by the four boilers on site). Fly ash production is estimated to have been 3310 kg/hr during the test period assuming a fly ash-to-bottom ash ratio of 4 and 99% ESP efficiency. The prescrubber slurry production rate was ≤ 11,300 kg/hr with an average solids content of 0.47%. No production rates are available for the ash pond sludge.

TABLE 28. ORGANICS IN THE LIQUID STREAMS*

Carbon Number	Concentration, g/m^3			
	Lake Water	Clarifier Overflow	City Water	Prescrubber Slurry Liquids
C_7	< 0.001	< 0.001	< 0.001	< 0.001
C_8	0.014	< 0.001	< 0.001	< 0.001
C_9	< 0.001	< 0.001	< 0.001	< 0.001
C_{10}	< 0.001	< 0.001	< 0.001	< 0.001
C_{11}	< 0.001	< 0.001	< 0.001	< 0.001
C_{12}	0.001	< 0.001	< 0.001	< 0.001
C_{13}	< 0.001	< 0.001	< 0.001	< 0.001
C_{14}	< 0.001	< 0.001	< 0.001	< 0.001
C_{15}	0.001	< 0.001	< 0.001	< 0.001
C_{16}	< 0.001	0.003	< 0.001	< 0.001
$>C_{16}$	0.219	0.105	0.073	0.351
Total	0.235-0.242	0.108-0.117	0.073-0.083	0.351-0.361

* Level 1 procedures were utilized.

The thiosulfate and melt tank purge streams are not waste streams by design. During normal operation, these streams would be dried and the solid by-product could be marketed to the pulp and paper industry. The production rate of these streams is approximately 5 kg/hr with 25 to 30% dissolved salts. Samples at the laboratory were found to contain up to 40% crystalline material.

This section presents the results of inorganic and organic analyses performed on these solid wastes and process solids. Coal analyses have been presented previously and will not be discussed in this section.

4.6.1 Inorganic Analyses

Concentrations of major and trace elements in the solids samples were primarily determined by ICP. Trace elements not determined by ICP are arsenic and antimony which were determined by atomic absorption, and mercury which was determined by cold vapor atomic absorption. Concentrations of 25 elements present in the solids are presented in Table 29. To assess the hazard potential of the waste streams, data for these streams are compared with the DMEG values for these elements. Analyses of the thiosulfate and melt tank purge streams are also compared with DMEG values because these streams were discharged to the ash pond during the test period.

The highest elemental concentrations were generally found in the fly ash, prescrubber solids and ash pond sludge which consist primarily of ash. From four to six elements in each of these streams exceeded their respective health-based DMEG values for solids. Eleven or twelve elements in each of these streams exceeded their respective ecology-based DMEG values for solids. Sulfate analyses of the fly ash and ash pond sludge indicate concentrations of 1.8 and 0.55% $SO_4^=$, respectively. No sulfate was detected in the prescrubber slurry solids. These data indicate that fly ash, prescrubber slurry solids and the ash pond sludge warrant disposal in a specially designed landfill.

Solids from the thiosulfate and melt tank purge streams appear to be relatively pure sodium salts. Only sodium exceeded its health-based DMEG value in these solids. Four elements in each of these solids exceeded their ecology-based DMEG values. Sulfate analyses (both sulfite and sulfate are reported as sulfate) indicate that solids from the thiosulfate purge contain 64.9% $SO_4^=$ and solids from the melt tank purge contain 65.5% $SO_4^=$. Sulfate and sodium concentration data indicate that the thiosulfate purge consists primarily of Na_2SO_3 (36.5% Na with a Na:S mole ratio of 2) while the melt tank solids consist primarily of $NaHSO_3$ (22.1% Na with a Na:S mole ratio of 1).

The soda ash and product sulfur streams were also found to be of high purity. No impurity was present in either solid at levels exceeding approximately 100 ppm and most impurities were present at levels below 10 ppm.

4.6.2 Organic Analyses

Organic analyses were performed on fly ash and ash pond sludge sample. Because of the extremely low solids concentration in the prescrubber slurry

TABLE 29. MAJOR AND TRACE ELEMENT CONCENTRATIONS IN PROCESS AND WASTE SOLIDS*

Element	DMEG Value, mg/kg		Fly Ash			Prescrubber Slurry Solids			Ash Pond Sludge		
	Health	Ecology	mg/kg	Discharge Severity Health	Discharge Severity Ecology	mg/kg	Discharge Severity Health	Discharge Severity Ecology	mg/kg	Discharge Severity Health	Discharge Severity Ecology
Al	16,000	200	38,000	2.4	190	36,600	2.3	183	28,400	1.8	140
As	50	10	85.8	1.7	8.6	52	1.0	5.2	71.5	1.4	7.2
B	9,300	5,000	2,610	0.28	0.52	182	0.020	0.036	1,480	0.16	0.30
Ba	1,000	500	212	0.21	0.42	110	0.11	0.22	602	0.60	1.2
Ca	48,000	3,200	44,900	0.94	14	3,510	0.073	1.1	25,500	0.53	8.0
Cd	10	0.2	<0.8	<0.08	<4	<0.8	<0.08	<4	<0.8	<0.08	<4
Co	150	50	26.1	0.17	0.52	19.9	0.13	0.40	15.7	0.10	0.31
Cr	50	50	32.1	0.46	0.46	38.0	0.76	0.76	5.7	0.11	0.11
Cu	1,000	10	32.5	0.032	3.2	12.6	0.013	1.3	15.1	0.015	1.5
Fe	300	50	141,000	470	2,800	90,800	300	1,800	41,600	49	290
Hg	2	50	0.28	0.1	0.0056	11.4	5.7	0.23	0.18	0.09	0.0036
K	‡	4,600†	2,120	---	0.46	2,305	---	0.50	1,080	---	0.23
La	340,000	‡	14.7	<0.001	---	0.4	<0.001	---	0.4	<0.001	---
Li	70	75	23.5	0.34	0.31	19.7	0.28	0.26	1.8	0.026	0.024
Mg	18,000	17,400	3,230	0.18	0.18	2,820	0.16	0.16	6,380	0.35	0.37
Mn	50	20	171	3.4	8.5	6.32	0.13	0.32	206	4.1	10.3
Na	160,000	‡	923	0.0058	---	887	0.0055	---	1,020	0.0063	---
Ni	45	2	78.4	1.7	39	47.3	1.1	24	7.8	0.17	3.9
P	3,000	0.1	571	0.19	6,000	<3.2	<0.0011	<30	1,250	0.42	1,000
Pb	50	10	94.1	1.9	9.4	80.8	1.6	8.1	<5.9	<0.12	<0.59
Sb	1,500	40	<0.2	<0.001	<0.005	<0.2	<0.001	<0.005	<0.2	<0.001	<0.005
Si	3,000	‡	110	0.037	---	<1.0	<0.001	---	12.7	0.0042	---
Sr	9,200	‡	118	0.013	---	<7.9	<0.001	---	343	0.037	---
V	500	30	135	0.27	4.5	49.3	0.099	1.6	76.8	0.15	2.6
Zn	5,000	20	629	0.13	31	709	0.14	35	235	0.047	12

(Continued)

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* Arsenic and antimony were determined by atomic absorption (Level 2) and mercury was determined by a cold vapor method (Level 1). All other elements were measured by ICP (Level 2).

† The ecology-based DMEG for potassium is based on ionic potassium.

‡ DMEG values have not been established for these elements.

TABLE 29. (Continued)

Element	Thiosulfate Purge Solids			Melt Tank Purge Solids			Soda Ash,	Product Sulfur
	mg/kg	Discharge Severity		mg/kg	Discharge Severity			
		Health	Ecology		Health	Ecology	mg/kg	mg/kg
Al	<2.0	<0.001	<0.01	<2.0	<0.001	<0.01	<2.0	<3
As	<0.4	<0.008	<0.04	<0.4	<0.008	<0.04	<0.4	<2
B	523	0.056	0.10	<0.6	<0.001	<0.001	<0.6	25.0
Ba	<2.0	<0.002	<0.004	<2.0	<0.0020	<0.0040	<2.0	<3
Ca	<1.2	<0.001	<0.001	<1.2	<0.001	<0.001	<1.2	<16
Cd	<0.8	<0.08	<4	0.80	0.080	4.0	<0.8	<0.7
Co	<1.0	<0.0067	<0.020	<1.0	<0.0067	<0.020	<1.0	<0.9
Cr	2.54	0.051	0.051	<1.2	0.024	0.024	<1.2	<1
Cu	<0.2	<0.001	<0.02	<0.2	<0.001	<0.02	<0.2	<22
Fe	228	0.76	4.6	<0.4	<0.0013	<0.0080	<0.4	<17
Hg	0.02	0.01	<0.001	0.008	0.004	<0.001	0.004	0.2
K	598	---	0.13	43.8	---	0.0095	<20	<10
La	<0.4	<0.001	---	<0.4	<0.001	---	<0.4	<0.3
Li	<2.0	<0.029	<0.027	10	0.14	0.13	<0.2	<10
Mg	49.9	0.0028	0.0029	<4.0	<0.001	<0.001	34.9	<8
Mn	<0.1	<0.0020	<0.005	<0.1	<0.0020	<0.0050	<0.1	<0.1
Na	333,000	2.1	---	211,000	1.3	---	438,000	100
Ni	<4.0	<0.089	<2	<4.0	<0.089	<2.0	<4.0	<20
P	<3.2	<0.0011	<30	<3.2	<0.0011	<32	<3.2	<3
Pb	<5.9	<0.12	<0.59	<6.0	<0.12	<0.60	<5.9	<5
Sb	9.3	0.0062	0.23	23	0.015	0.57	0.37	6.25
Si	206	0.067	---	<0.1	<0.001	---	117	<1
Sr	<7.9	<0.001	---	<8.0	<0.001	---	<7.9	<7
V	<0.4	<0.001	<0.013	<0.4	<0.001	<0.013	<0.4	<0.3
Zn	4.61	<0.001	0.23	109	0.022	5.4	<0.8	<3

(0.47% average solids), insufficient material was available for organic analyses. Concentrations of C_7 - C_{16} organics and higher molecular weight organics ($>C_{16}$) measured in the solid wastes are presented in Table 30. Total organics in the fly ash and ash pond sludge consisted primarily of higher molecular weight organics. The C_7 - C_{16} organics were present in the fly ash and ash pond sludge at concentrations of 0.345 and 0.245 mg/kg, respectively, while higher molecular organics were present at concentrations of 4.42 and 4.48 mg/kg, respectively. An erroneously high C_8 fraction was determined in the ash pond sludge as a result of an acetone rinse prior to extraction; this material was not included in the C_7 - C_{16} and total organics computations.

Although no specific organic compounds were identified in the solid wastes, IR analyses indicate the presence of saturated hydrocarbons, aromatics, esters, and ethers. The fly ash also contained ketones and the ash pond sludge contained unsaturated hydrocarbons and alcohols. Detailed IR analytical results are presented in Appendix C. GC/MS analysis with a detection limit of 20 μg/kg did not reveal the presence of any POM.

TABLE 30. ORGANIC ANALYSES OF SOLID WASTES*

Carbon Number	Concentration, mg/kg	
	Fly Ash	Ash Pond Sludge
C_7	< 0.001	0.168
C_8	< 0.001	2.08†
C_9	< 0.039	< 0.001
C_{10}	0.033	0.050
C_{11}	0.079	< 0.001
C_{12}	0.037	< 0.001
C_{13}	0.019	0.006
C_{14}	0.023	0.006
C_{15}	0.018	0.015
C_{16}	0.102	< 0.001
$>C_{16}$	4.42	4.48
Total	4.76‡	4.73‡

*Level 1 procedures were utilized.

†GC-MS analysis showed the TCO C_8 material to be acetone condensation products, and this value is not included in the TCO total. This ash pond sludge was received wet from the field and required an acetone rinse prior to Soxhlet extraction.

‡This sample exceeds the 1.0 mg/kg criterion for LC; however, the minimum sample size recommended for LC by the Level 1 Procedures Manual is 15 mg and less than 3 mg were available for analysis.

REFERENCES

1. Demonstration Test Plan, Test and Evaluation Program For The NIPSCO/ Davy/Allied Demonstration Plant. Report prepared by TRW Environmental Engineering Division, Energy Systems Group for the U.S. Environmental Protection Agency Under Contract No. 68-02-1877/Task 1. March 1976.

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3. Compilation of Air Pollution Emission Factors, AP-42, Part A. Third Edition. U.S. Environmental Protection Agency. August 1977.

4. Cheney, J.L. and J.B. Homolya. Sampling Parameters for Sulfate Measurement and Characterization. Environmental Science and Technology 13(5): 584-588. May 1979.

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APPENDIX A

ANALYTICAL PROCEDURES APPLIED TO NIPSCO SAMPLES

With a few exceptions discussed below, the samples were prepared and extracted according to the procedures in Emissions Assessment of Conventional Stationary Combustion Systems: Methods and Procedures Manual for Sampling and Analysis (EACCS), EPA-600/7-79-029a. The overall inorganic analysis scheme is presented in Figure A-1 and the organic analysis scheme in Figures A-2 and A-3. The numerical references in Figures A-2 and A-3 are references to the EACCS manual.

Inorganic Analyses

Most trace elements were analyzed by Inductively Coupled Optical Emission Spectroscopy (ICP). ICP is a flame emission technique in which atoms are thermally excited to emit light at their characteristic wavelengths. In practice, samples in the form of a liquid are aspirated into the atomizer. The atomization and excitation source is a plasma torch whose temperature is on the order of 7000°K. The entire instrument is controlled by a mini-computer, which can store calibration curves and calculate solution concentrations directly. Sensitivities are on the order of 0.1 μg/ml to 1.0 μg/ml. These analyses are vended and analytical procedures are not detailed here.

ICP was supplemented with cold vapor UV analysis for mercury (EACCS 8.4) and graphite furnace atomic absorption analyses using standard addition for arsenic and antimony (Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority pollutants, April, 1977, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268). The graphite furnace method was selected for these samples because of its better sensitivity than the hydride generation method.

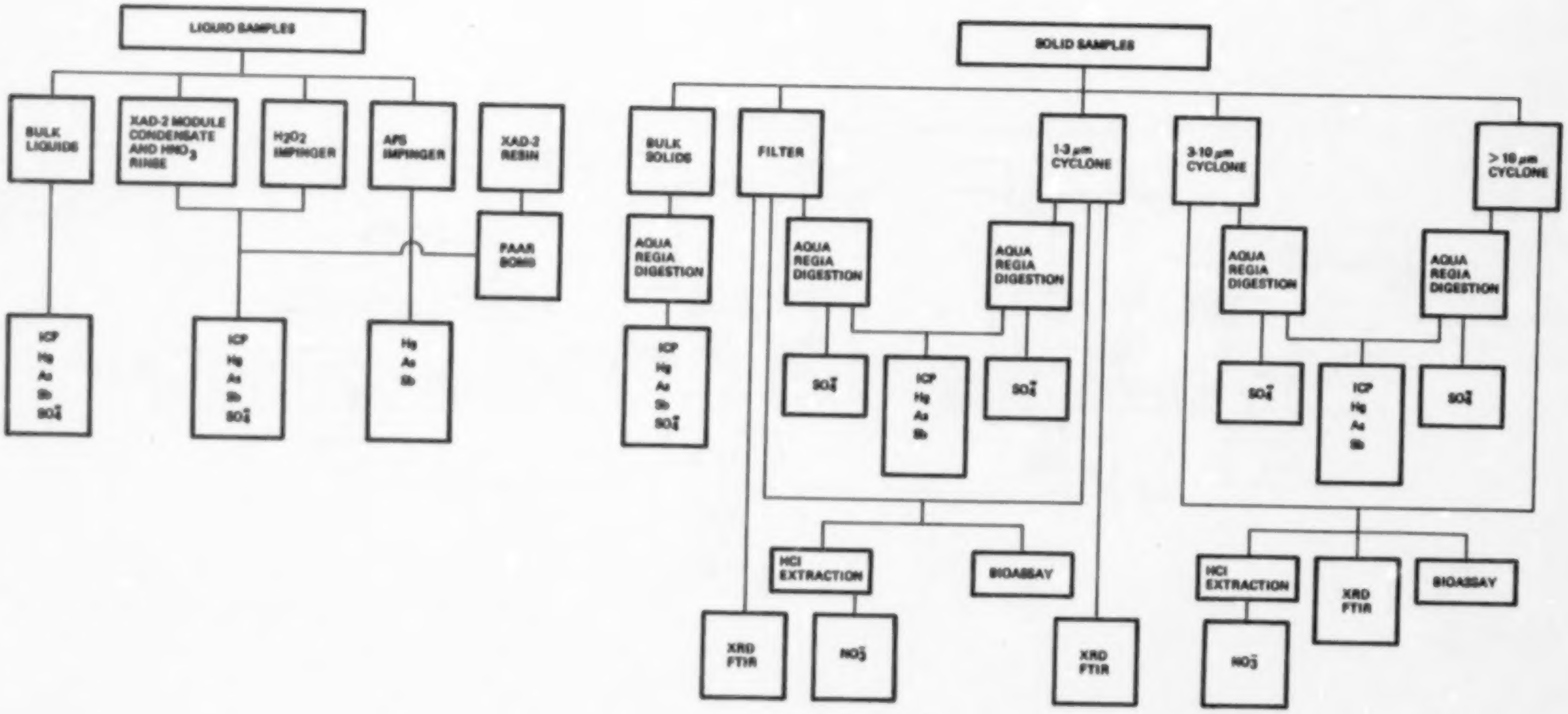
LIQUID SAMPLES
BULK LIQUIDS
XAD-2 MODULE CONDENSATE AND HNO_3 RINSE
H_2O_2 IMPINGER
APS IMPINGER
XAD-2 RESIN
PAAR BOMB
ICP
Hg
As
Sb
$SO_4^=$
ICP
Hg
As
Sb
$SO_4^=$
Hg
As
Sb
SOLID SAMPLES
BULK SOLIDS
FILTER
1-3 µm CYCLONE
3-10 µm CYCLONE
> 10 µm CYCLONE
AQUA REGIA DIGESTION
ICP
Hg
As
Sb
$SO_4^=$
AQUA REGIA DIGESTION
AQUA REGIA DIGESTION
$SO_4^=$
ICP
Hg
As
Sb
$SO_4^=$
AQUA REGIA DIGESTION
AQUA REGIA DIGESTION
$SO_4^=$
ICP
Hg
As
Sb
$SO_4^=$
HCl EXTRACTION
BIOASSAY
XRD FTIR
NO_3^-
XRD FTIR
HCl EXTRACTION
XRD FTIR
BIOASSAY
NO_3^-

Figure A-1. Inorganic Analyses Flow Chart

Reproduced from
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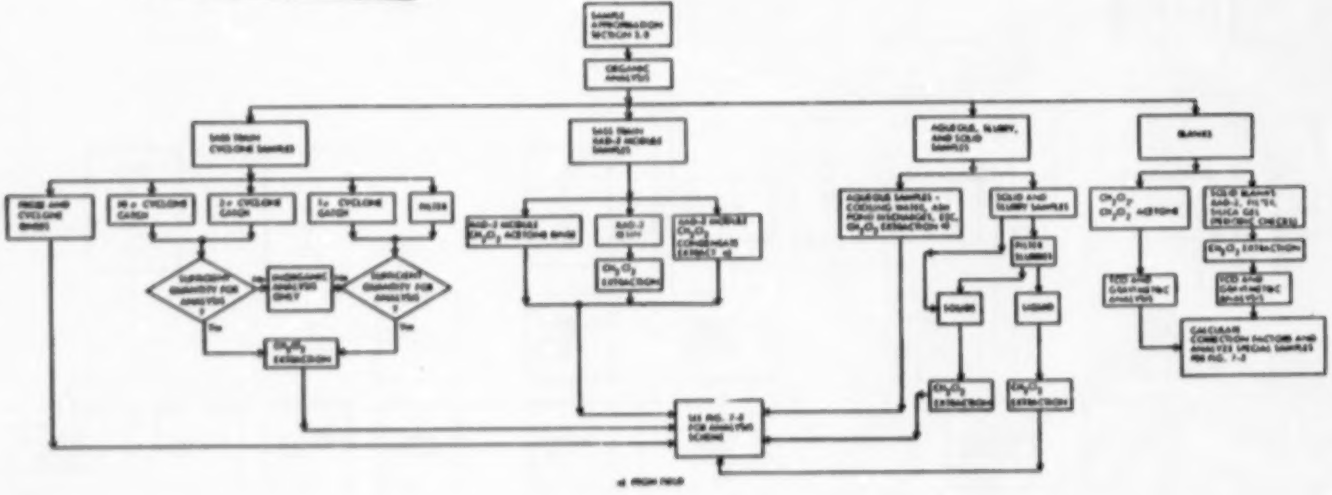

SAMPLE ACQUISITION SECTION 3.0
ORGANIC ANALYSIS
SASS TRAIN CYCLONE SAMPLES
PROBE AND CYCLONE RINSES
10 μ CYCLONE CATCH
3 μ CYCLONE CATCH
1 μ CYCLONE CATCH
FILTER
SUFFICIENT QUANTITY FOR ANALYSIS ?
INORGANIC ANALYSIS ONLY
SUFFICIENT QUANTITY FOR ANALYSIS ?
Yes
Yes
CH2Cl2 EXTRACTION
SASS TRAIN XAD-2 MODULE SAMPLES
XAD-2 MODULE CH2Cl2 ACETONE RINSE
XAD-2 RESIN
CH2Cl2 EXTRACTION
XAD-2 MODULE CH2Cl2 CONDENSATE EXTRACT
SEE FIG. 7-8 FOR ANALYTIC SCHEME
AQUEOUS, SLURRY, AND SOLID SAMPLES
AQUEOUS SAMPLES - COOLING WATER, ASH POND DISCHARGES, ETC. CH2Cl2 EXTRACTION
SOLID AND SLURRY SAMPLES
FILTER SLURRIES
SOLIDS
LIQUID
CH2Cl2 EXTRACTION
CH2Cl2 EXTRACTION
BLANKS
CH2Cl2, CH2Cl2 ACETONE
SOLID BLANKS XAD-2, FILTER, SILICA GEL (REAGENT CHECKS)
CH2Cl2 EXTRACTION
TCO AND GRAVIMETRIC ANALYSIS
TCO AND GRAVIMETRIC ANALYSIS
CALCULATE CORRECTION FACTORS AND ANALYZE SPECIAL SAMPLES PER FIG. 7-8

Figure A-2. Level 1 Organic Analysis Flow Chart

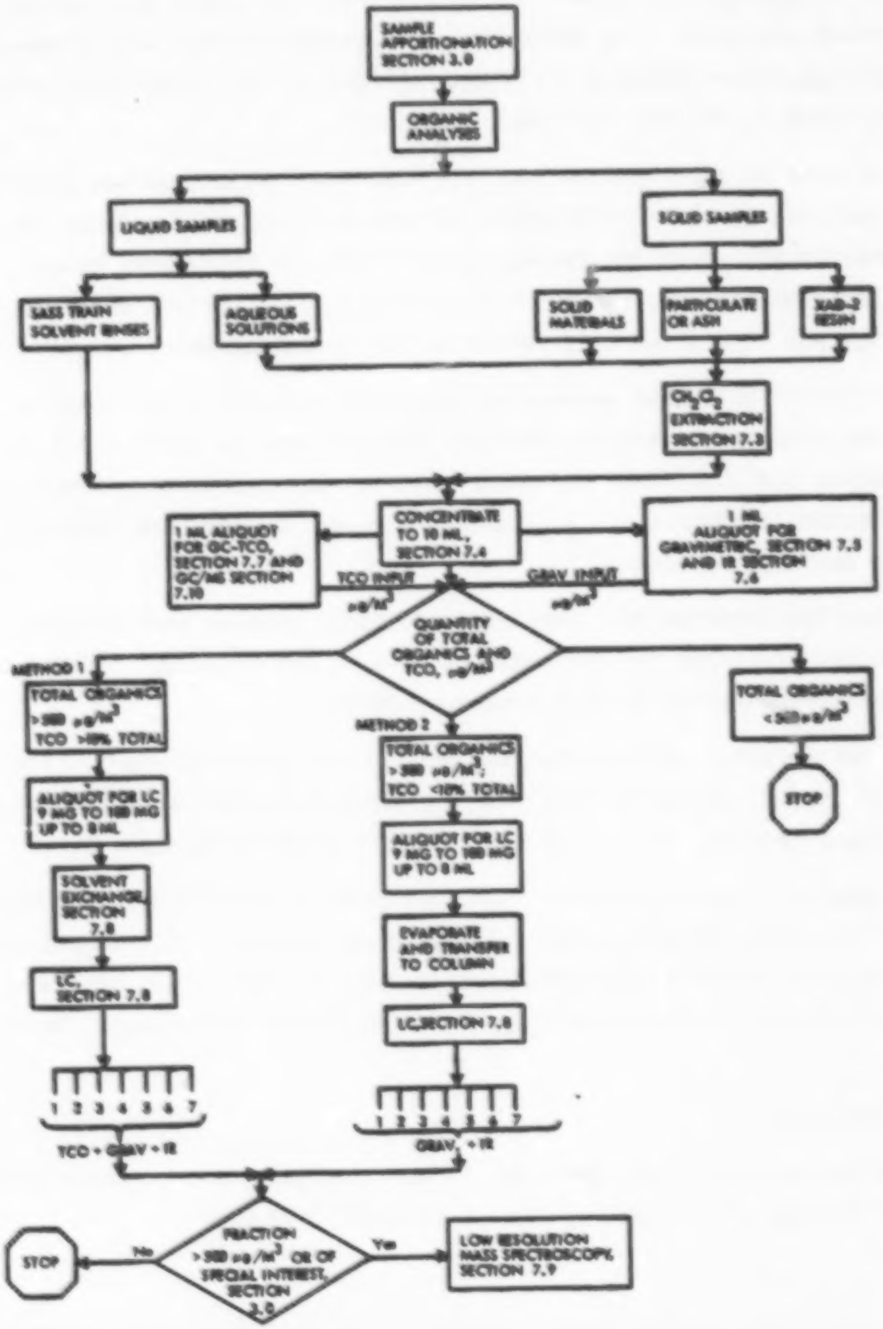

SAMPLE APPORTIONATION SECTION 3.0
ORGANIC ANALYSES
LIQUID SAMPLES
SOLID SAMPLES
SASS TRAIN SOLVENT RINSES
AQUEOUS SOLUTIONS
SOLID MATERIALS
PARTICULATE OR ASH
XAD-2 RESIN
CH2Cl2 EXTRACTION SECTION 7.3
CONCENTRATE TO 10 ML, SECTION 7.4
1 ML ALIQUOT FOR GC-TCO, SECTION 7.7 AND GC/MS SECTION 7.10
1 ML ALIQUOT FOR GRAVIMETRIC, SECTION 7.5 AND IR SECTION 7.6
TCO INPUT μg/M3
GRAV INPUT μg/M3
QUANTITY OF TOTAL ORGANICS AND TCO, μg/M3
METHOD 1
TOTAL ORGANICS >500 μg/M3 TCO >10% TOTAL
METHOD 2
TOTAL ORGANICS >500 μg/M3; TCO <10% TOTAL
TOTAL ORGANICS <500 μg/M3
STOP
ALIQUOT FOR LC 9 MG TO 100 MG UP TO 8 ML
SOLVENT EXCHANGE, SECTION 7.8
LC, SECTION 7.8
EVAPORATE AND TRANSFER TO COLUMN
LC,SECTION 7.8
1 2 3 4 5 6 7
1 2 3 4 5 6 7
TCO + GRAV + IR
GRAV. + IR
FRACTION >500 μg/M3 OR OF SPECIAL INTEREST, SECTION 3.0
No
Yes
STOP
LOW RESOLUTION MASS SPECTROSCOPY, SECTION 7.9

Figure A-3. Level 1 Organic Analysis Methodology

Aqua regia digestion (EACCS 8.2.2) was used to prepare most solids for trace element analysis. The XAD-2 resin and product sulfur were prepared by Paar bomb combustion (EACCS 8.2.1), and the coal by low temperature plasma ashing followed by HF-HNO_3 Parr bomb combustion.

An aliquot of each SASS particulate aqua regia digestate was used for sulfate analysis by the turbidimetric procedure (EACCS 8.7). These results were cross-checked on an ion chromatograph (IERL-TRP Procedures Manual: Level 1 Environmental Assessment, EPA-600/7-78-201). Sulfate analyses on bulk solids and liquids were performed by ion chromatography.

The hydrochloric acid extraction procedure used for preparation of SASS particulate samples for nitrate analysis was the same as EACCS 8.8.2, with the exception that 0.01M HCl was used. Nitrate was analyzed by ultraviolet spectrophotometry (Method 419 A, Standard Methods for the Examination of Water and Wastewater, 14th ed.)

Controlled Condensation Sampling Train (CCS) samples were analyzed by ion selective electrode for fluoride (EACCS 8.9) and chloride (EACCS 8.10) and by the turbidimetric sulfate procedure (EACCS 8.7).

All MRI impactor sulfate analyses were by ion chromatography. The procedure for removal of the sulfate from the Apiezon-coated impactor plates was developed recently at TRW, and details are given in Appendix B.

The powder X-ray diffraction (XRD) analysis is described in the EPA/IERL-RTP Procedures Manual: Level 2 Sampling and Analysis of Oxidized Inorganic Compounds, EPA-600/2/79-200, Section 3.2. A description of Fourier Transform Infrared (FTIR) methodology is given in the same manual, Section 3.1.

Organic Analyses

Samples acquired at Mitchell No. 11 were analyzed in accordance with the EACCS Methods and Procedures Manual (EPA-600/7-79-029a).

Bioassay

All SASS train samples were returned to TRW for preparation prior to testing by the bioassay contractor. Approximately 120 m^3 of gas was sampled as a combined Level 1/Bioassay sample. A fresh cannister of XAD-2 resin was used on each of the four sampling days, and the resins extreacted by the normal procedure (EACCS 7.4). The extracts and module rinse were combined and concentrated, and three-fourths of the sample removed for bioassay.

Cyclones and filter particulate catches were dessicated and weighed to constant weight and then portions combined to form the following two fractions for bioassay: $>3\mu$ particulate and $<3\mu$ particulate.

APPENDIX B

PROCEDURES FOR ANALYSIS OF SULFATE ON MRI IMPACTOR PLATES

EQUIPMENT

(1) Petri Dishes; obtain 7 small (50 mm diameter) petri dish covers or bottoms and mark them sequentially, using a diamond stylus or vibrating etcher. Do not use pencil or grease pen as they will be removed during plasma ashing.

(2) Low Temperature Plasma Asher (LTA); International Plasma Corporation Model PM104B unit or equivalent.

(3) Drying Oven; capable of 100°C ± 5°C.

(4) Steam Bath.

REAGENTS

(1) Toluene; ACS reagent grade minimum.

(2) Sodium Carbonate Solution; dissolve 40 gms of Na_2CO_3 in 1 liter of deionized water. 1.0 ml = 40 mg Na_2CO_3.

(3) Hydrochloric acid; 0.01 M HCl; 0.83 ml conc. HCl diluted to 1 liter.

CLEANING

It is very important that all glassware used in this procedure be precleaned with 1+1 HNO_3 acid. Special emphasis should be given to the cleaning of the petri dishes, since both internal and external surfaces may be contacted by the extracting solvent.

PROCEDURE

(1) Perform all extractions and evaporations of toluene in fume hood and do not allow open flames in the work area.

(2) Turn on steam bath (low or med. heat) inside fume hood, allowing it to heat while carrying out the following steps. Adjust drying oven to 80°C ± 5°C.

(3) Obtain a group of impactor discs; for optimum organization it is suggested that the discs are handled in groups of seven, as they are arranged in the impactor assembly.

(4) Carefully pipet 1.0 ml of toluene, using a disposable Pastuer pipet, into each of the impactor discs to dissolve the Apiezon L grease. Allow the toluene to contact the discs, inside the designated petri dish, for about a minute.

(5) Carefully transfer the toluene - Apiezon L solution from the impactor disc into the appropriate petri dish, rinsing the disc with two 1.0 mL volumes of toluene.

(6) Add another portion of toluene, as in Step 4, to impactor disc.

(7) Transfer, as in Step 5.

(8) Repeat the dissolution and transfer steps until the Apiezon L grease and any particulate material is completely transferred from the impactor disc into the petri dish. If any remaining Apiezon L grease adheres to the disc, scrape with a stainless steel or teflon spatula (not a rubber policeman) and rinse again with toluene.

(9) Gently warm the petri dish containing the toluene - Apiezon L solution over a steam bath until the solvent has completely evaporated. Rotate the petri dish while evaporating the toluene to create an even layer of Apiezon L and particulate. (Caution: do not overheat, as this will cause Apiezon L to darken).

(10) Add 1.0 ml of 40 mg/ml Na_2CO_3 solution to each petri dish and distribute the solution evenly over the Apiezon covered portion of the internal surface. Dry in an 80°C oven until the water has evaporated.

(11) Following the instructions supplied in the instrument operating manual, tune the low temperature plasma asher to optimize operation.

(12) Remove the prepared petri dishes from the drying oven and allow to cool.

(13) Place the cooled petri dishes in the low temperature plasma asher and subject them to low temperature ashing for 24 hours or until the Apiezon L is completely oxidized.

(14) When ashing step has been completed, carefully remove the petri dishes from LTA and allow to cool. The ash produced in this step is very light and is easily lost if exposed to air currents.

(15) Carefully rinse the ash from the petri dish into a 150 ml beaker, using 50 ml of 0.01 M HCl.

(16) If the ash adheres to the internal surface of petri dish, the entire dish may be submerged in 0.01 M HCl, in a 250 ml beaker, to accomplish dissolution.

(17) After bringing the 0.01 M HCl solution to a gentle boil, cover beaker with a watch glass, and allow to boil for 2 hours. It will be necessary to add deionized water to maintain the proper volume.

(18) Make note of any suspended or insoluble material observed during and after digestion.

(19) When digestion is completed, remove beaker from hot plate and cool. Filter sample with a #41 Whatman filter pad and dilute to a volume of 50.0 ml.

(20) Determine sulfate on the sample extract using ion chromatography.

(21) Blanks and standards (produced by pipetting a standard Na_2SO_4 solution onto unused impactor plates) should be run with the first group of samples and every fifth group thereafter.

(22) Calculations

$$\text{mg sulfate} = A \times B$$

where A = ppm sulfate in solution
B = final solution volume from step 19, Liters).

APPENDIX C

RESULTS OF INFRARED ANALYSES

TABLE C-1. INTERPRETATION OF INFRARED SPECTRA OF SAMPLE CONCENTRATES

Sample	Band Location cm^{-1}	Band Intensity	Assignment	Comments
164-XMCD-SE-KD-GI	3220	W	OH, water, alcohol	
Air heater inlet	3030	W	Unsaturated CH	
	2960	M	Saturated CH	
	2920	M	Saturated CH	
	2864	M	Saturated CH	
	1720	M	Esters, -C=O	
	1600	W	Aromatic, C=C	
	1570	W	Fused ring breathing	
	1450	W	Saturated CH	
	1372	W	Saturated CH	
	1270	W	Ester, phenol	
	1250	W	Ester, phenol	
	1105	M	Ether, C-O of alcohol	
	940	W	H or C=C, benzene ring substitution	
	850	W	H deformations aromatic hydrocarbons	
	760	W	H deformations aromatic hydrocarbons	
	720	W	H deformations aromatic hydrocarbons	
165-XMCD-SE-KD-GI	3030	W	Aromatic CH	
Scrubber inlet	2962	M	Saturated CH	
	2922	M	Saturated CH	
	2862	M	Saturated CH	
	1720	M	Esters, C=O	
	1602	W	Aromatic, C=C	
	1560	W	Fused ring breathing	
	1450	W	Saturated CH	
	1375	W	Saturated CH	
	1260	W	Ester, phenol, C-O	
	1100	M	Ether, C-O	
	950	W	Aromatic hydrocarbons	
	855	W	Aromatic hydrocarbons	
	800	W	Aromatic hydrocarbons	
	760	W	Aromatic hydrocarbons	
	705	W	Aromatic hydrocarbons	
166-XMCD-SE-KD-GI	2960	M	Saturated CH	
Scrubber outlet	2922	M	Saturated CH	
	2864	M	Saturated CH	
	1725	M	Esters, C=O	
	1605	W	Aromatic, C=C	

(Continued)

TABLE C-1. (Continued)

Sample	Band Location cm^{-1}	Band Intensity	Assignment	Comments
166-SMCD-SE-KD-GI Scrubber outlet (Continued)	1555	W	Aromatic, ring breathing	
	1450	W	Saturated CH	
	1372	W	Saturated CH	
	1265	W	Esters, C-O	
	1102	M	Ether, C-O	
	940	W	Aromatic hydrocarbons	
	850	W	Aromatic hydrocarbons	
	800	W	Aromatic hydrocarbons	
	755	W	Aromatic hydrocarbons	
	700	W	Aromatic hydrocarbons	
164/6 XRB-SE-KD-GI XAD-2 Resin Blank	2962	W	Saturated CH	
	2922	M	Saturated CH	
	2864	M	Saturated CH	
	1722	W	Ester, C=O	
	1455	W	Saturated CH	
	1372	W	Saturated CH	
	1350	W	Saturated CH	
	1275	W	Esters, C-O	
	1105	S	Ether, C-O	
	935	W	Aromatic rings	
	855	W	Aromatic rings	
164-PR-KD-GI	2920	M	Saturated CH (very weak scan)	
	2850	M	Saturated CH	
	1725	W	Esters	
	1695	W	Acid, aryl ketone	
	1462	W	Saturated CH	
	1375	W	Saturated CH	
	1275	W	Esters, C-O	
	1120	W	Esters, C-O	
	1080	W	Esters, C-O	
164/6-12-OR-SE-GI Fly ash	2960	M	Saturated CH	
	2920	M	Saturated CH	
	2848	M	Saturated CH	
	1730	W	Ester, C=O	
	1710	W	Ketone, C=O	
	1650	W	Aromatic, C=C	
	1540	W	Aromatic	
	1460	W	Saturated CH	
	1378	W	Saturated CH	

(Continued)

TABLE C-1. (Continued)

Sample	Band Location cm^{-1}	Band Intensity	Assignment	Comments
164/6-12-OR-SE-GI Fly ash (Continued)	1270	W	C-O, Ester	
	1125	W	C-O, Ether	
	960	W	C=C, Aromatic H deformation	
164/6-15-OR-SE-GI Ash pond sludge	3340	W	OH, water, alcohol	Broad (weak scan)
	3030	W	Unsaturated CH	
	2958	M	Saturated CH	
	2920	M	Saturated CH	
	1720	W	Ester	
	1670	W	C=C	
	1455	W	Saturated CH	
	1378	W	Saturated CH	
	1175	W	C-O-, ether, ester	
	1125	W	C-O-	
	1040	W	Aromatics	
	1010	W	Aromatics	

TABLE C-2. INTERPRETATION OF INFRARED SPECTRA OF LIQUID CHROMATOGRAPHY FRACTIONS

Sample	Band Location cm^{-1}	Band Intensity	Assignment	Comments
164-XMCD LC #1	2950	W	Saturated CH	
	2920	M	Saturated CH	
	2842	W	Saturated CH	
	1460	W	Saturated CH	
	1378	W	Saturated CH	
164-XMCD LC #2	3400	W	Water	Broad
	2960	M	Saturated CH	
	2922	S	Saturated CH	
	2850	M	Saturated CH	
	1725	M	Ester C=O	
	1640	W	Aromatic, C=C	
	1602	W	Aromatic, C=C	
	1462	W	Saturated CH	
	1450	W	Saturated CH	
	1372	W	Saturated CH	
	1275	W	Esters, C-O	
	1120	W	Esters, C-O	
	1070	W	Esters, C-O	
	740	W	Aromatic Rings	
	700	W	Aromatic Rings	
164-XMCD LC #3	2960	M	Saturated CH	
	2920	M	Saturated CH	
	2850	M	Saturated CH	
	1722	M	C=O Esters	
	1670	W	Carbonyl	
	1640	W	C=C	
	1600	W	Aromatic, C=C	
	1535	W	Aromatic, C=C	
	1450	W	Saturated CH	
	1378	W	Saturated CH	
	1270	M	Ester, C-O	
	1172	W	Ester, C-O	
	1118	W	Ester, C-O	
	1068	W	Ester, C-O	
	755	W	Hydrogen on aromatic ring	
	695	W	Hydrogen on aromatic ring	
164-XMCD LC #4	2960	M	Saturated CH	
	2920	M	Saturated CH	
	2850	M	Saturated CH	

(Continued)

TABLE C-2. (Continued)

Sample	Band Location cm^{-1}	Band Intensity	Assignment	Comments
164-XMCD LC#4 (Continued)	1725	M	Esters, C=O	
	1600	W	Aromatic, C=C	
	1450	W	Saturated CH	
	1370	W	Saturated CH	
	1270	W	-C-O-	
	1175	W	-C-O-	
	1112	W	Phthalate ester	
	1070	W	Phthalate ester	
	700	W	Aromatic rings	
164-XMCD LC #6	3400	W	Water, alcohol	
	3240	W	OH	
	2960	W	Saturated CH	
	2920	M	Saturated CH	
	2862	W	Saturated CH	
	1715	S	C-O, esters	
	1600	W	Aromatic, C=C	
	1450	W	Saturated CH	
	1375	W	Saturated CH	
	1250	W	-C-O-, esters	
	1100	M	Ether, C-O, alcohol	
	940	W	Aromatic hydrocarbons	
	755	W	Aromatic hydrocarbons	
	710	W	Aromatic hydrocarbons	
164-XMCD LC #7	3400	W	Water, acid, alcohol	Broad
	2960	M	Saturated CH	
	2922	M	Saturated CH	
	2862	M	Saturated CH	
	1720	W	Ester	
	1710	W	Ketone, acid	
	1600	W	Aromatic, C=C	
	1460	W	Saturated CH	
	1450	W	Saturated CH	
	1370	W	Saturated CH	
	1250	W	Ester, C-O	
	1100	M	Ether, C-O, alcohol	
	980	W	Aromatic hydrocarbons	
	800	W	Aromatic hydrocarbons	
	760	W	Aromatic hydrocarbons	
	705	W	Aromatic hydrocarbons	

(Continued)

TABLE C-2. (Continued)

Sample	Band Location cm^{-1}	Band Intensity	Assignment	Comments
164/6-XRB-LC #6 XAD-2 resin blank	3450	W	Water, alcohol	Broad
	2962	M	Saturated CH	
	2922	M	Saturated CH	
	2862	M	Saturated CH	
	1722	W	C=O, esters	
	1455	W	Saturated CH	
	1372	W	Saturated CH	
	1348	W	Saturated CH	
	1295	W	Ester, C-O	
	1250	W	Ester, C-O	
	1108	S	Ether, C-O, alcohol	
	935	W	Hydrogen on C=C	
	855	W	Hydrogen on C=C	
	760	W	Aromatic ring	
	710	W	Aromatic ring	
164/6-XRB-LC #7 XAD-2 resin blank	3400	W	Water, alcohol	Broad
	2961	W	Saturated CH	
	2922	M	Saturated CH	
	2862	M	Saturated CH	
	1722	W	C=O Ester, acid	Broad
	1660	W	C-O-C=O	
	1600	W	Aromatic, C=C	
	1560	W	Aromatic, COO^- Acid	
	1450	W	Saturated CH	
	1372	W	Saturated CH	
	1347	W	Saturated CH	
	1300	W	-C-O Ester	
	1250	W	-C-O Ester	
	1100	S	Ether, alcohol	
	940	W	Hydrogens on C=C	
	840	W	Hydrogens on C=C	

APPENDIX D

FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR) ANALYSIS OF FLUE GAS PARTICULATE SAMPLES FROM NIPSCO

INTRODUCTION

Particulate samples collected with the SASS train at the NIPSCO Mitchell No. 11 boiler/FGD system were analyzed by a Nicolet 7000 FTIR for specific compound identification. FTIR was used instead of conventional IR techniques because it offers improved sensitivity and data manipulation capabilities. Because FTIR uses an interferometer rather than a monochromator to separate wavelength, an interferogram is produced and then reduced to a wavelength vs. energy plot using a Fourier Transform. The spectra produced in this fashion is digitalized and can be stored in a computer for later manipulation. During this program, spectra of $NaHCO_3$, $NaHSO_4$, Na_2CO_3, $NaHSO_3$, Na_2SO_3, and $CaSO_4$ were stored in the computer and were available for electronic addition to the sample spectra. This "spiking" procedure facilitates the identification of IR bands associated with any of those compounds.

One milligram aliquots of loose particulate samples were mixed with 2.5 g of KBr in an agate mortar and pestle. Using a vacuum press, these samples were pressed into 10 mm diameter pellets of approximately 1 mm thickness. It was originally planned to obtain spectra of the particulate matter impacted on the glass fiber filter using a KRS-5 ATR cell. The filter background would then be subtracted from the sample spectra using the FTIR computer. Although this procedure worked well in the past, poor quality spectra were obtained. Fortunately, most of the filter samples had a layer of impacted particulate matter which could be removed using a scalpel. In the case of 166-PF (scrubber outlet particulate filter), a small amount of the glass fiber filter was removed with the particulate matter. In this case, a small amount of the glass fiber filter was placed in a KBr pellet, run on the FTIR and then was subtracted from the 166-PF spectra to leave only the bands associated with the particulate matter. All samples were run from 400 to 4000 cm^{-1}. Table D-1 lists the samples analyzed.

TABLE D-1. PARTICULATE SAMPLES ANALYZED BY FTIR

Sample Number	Location	Description
164-CC	Air heater inlet	Proportioned combination of 10 and 3 μm cyclone catches
165-CC	Scrubber inlet	
164-1C	Air heater inlet	1 μm cyclone catch
165-1C	Scrubber inlet	
164-PF	Air heater inlet	Particulate matter collected by the filter
165-PF	Scrubber inlet	
166-PF	Scrubber outlet	

The standard approach was to look at the FTIR spectra in the region of 400-1400 cm^{-1}, primarily focusing on the 400 to 900 cm^{-1} region. This is where most of the inorganic bands lie. Typically anion types (sulfate, oxide) were recognized first. Comparison of the unknown spectra with spectra of standards prepared by TRW (Figures D-1 through D-6) or with reference spectra (Nyquist and Kagel "Infrared Spectra of Inorganic Compounds") aided in the exact compound identification. Additional guidance was provided by the elemental data for the particulate catches. Spectra were generally very weak. Without the stability of FTIR and its computer-assisted spectra magnification, little or no information would have been obtained.

One problem in identifying fly ash components is that mineral matter present in the coal often has an amorphous structure after firing; this tends to hamper clear identification of the original mineral. In cases where bands appear in regions known for silicate minerals, a general term "silicate matrix" will be applied. A discussion of each sample follows and their IR spectra from 400 to 900 cm^{-1} are presented.

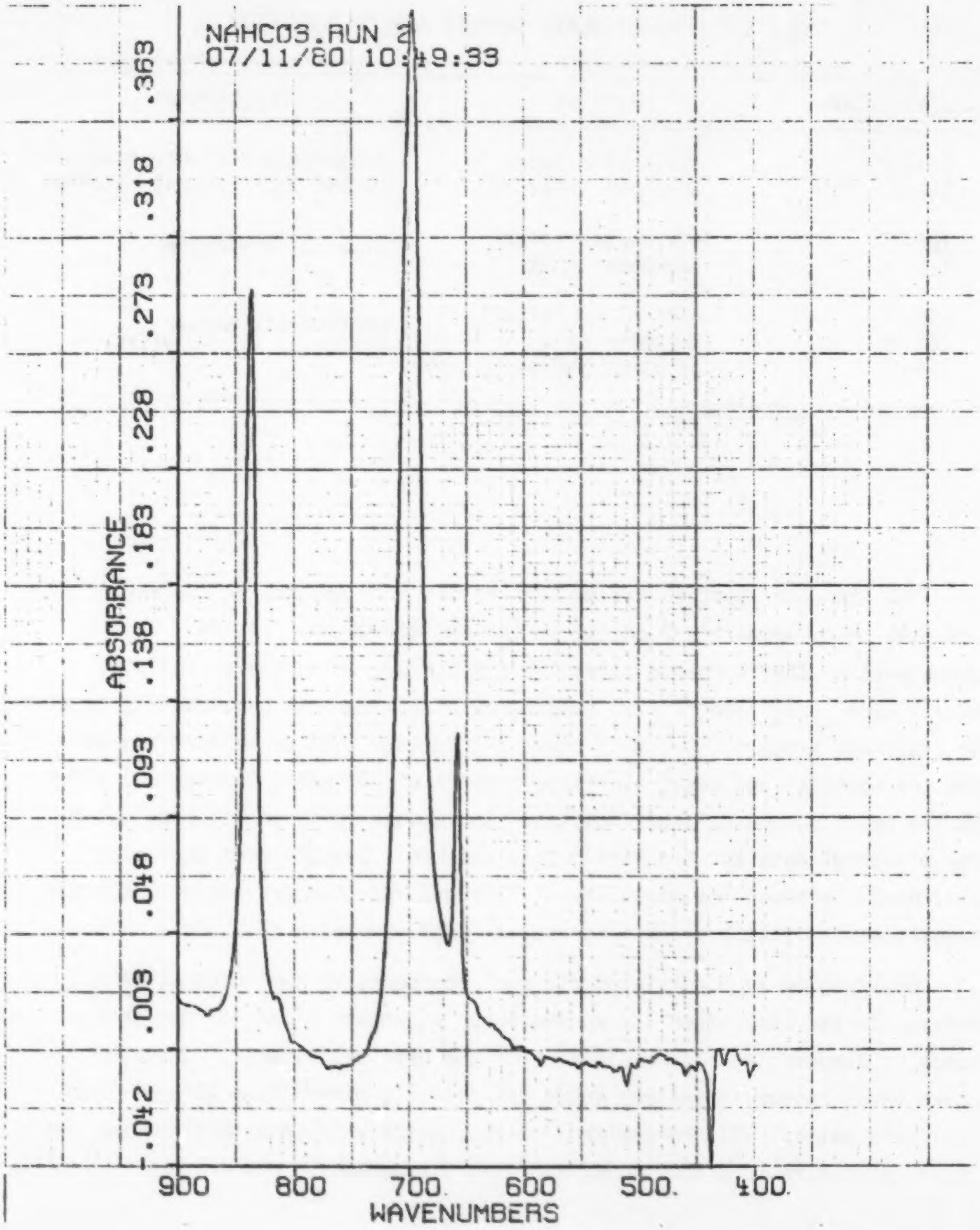


Figure D-1. Sodium Bicarbonate Standard

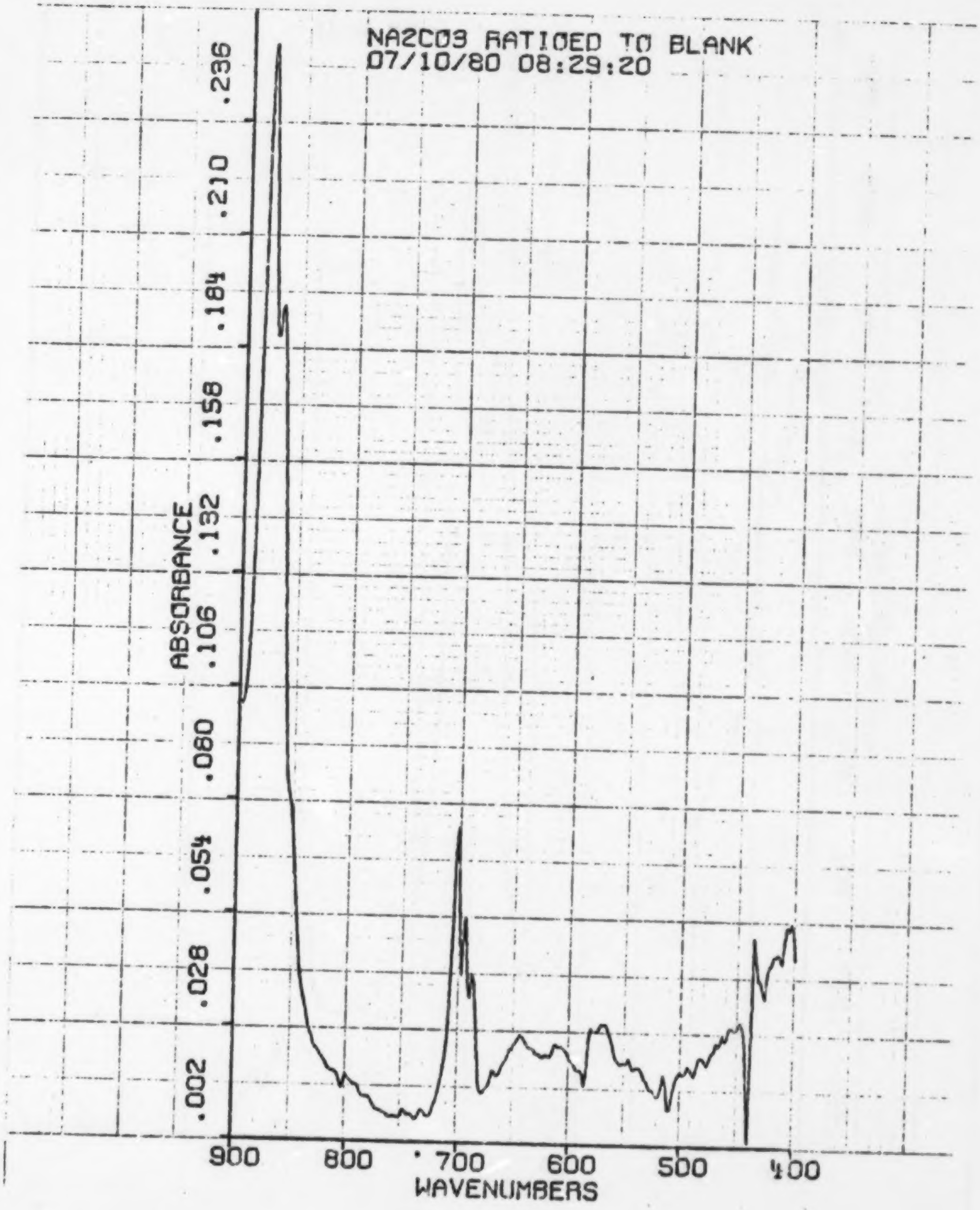


Figure D-2. Sodium Carbonate Standard

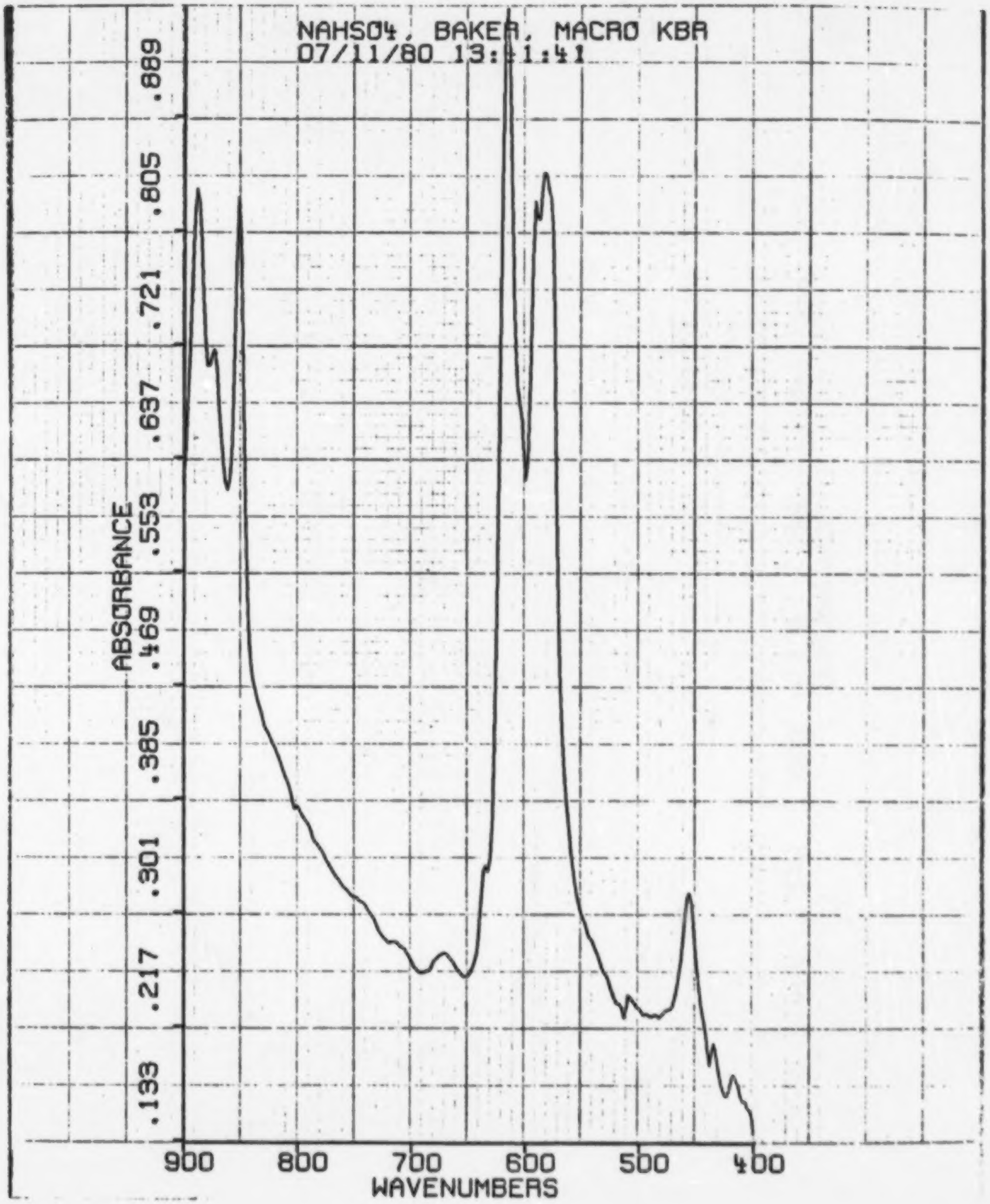


Figure D-3. Sodium Bisulfate Standard

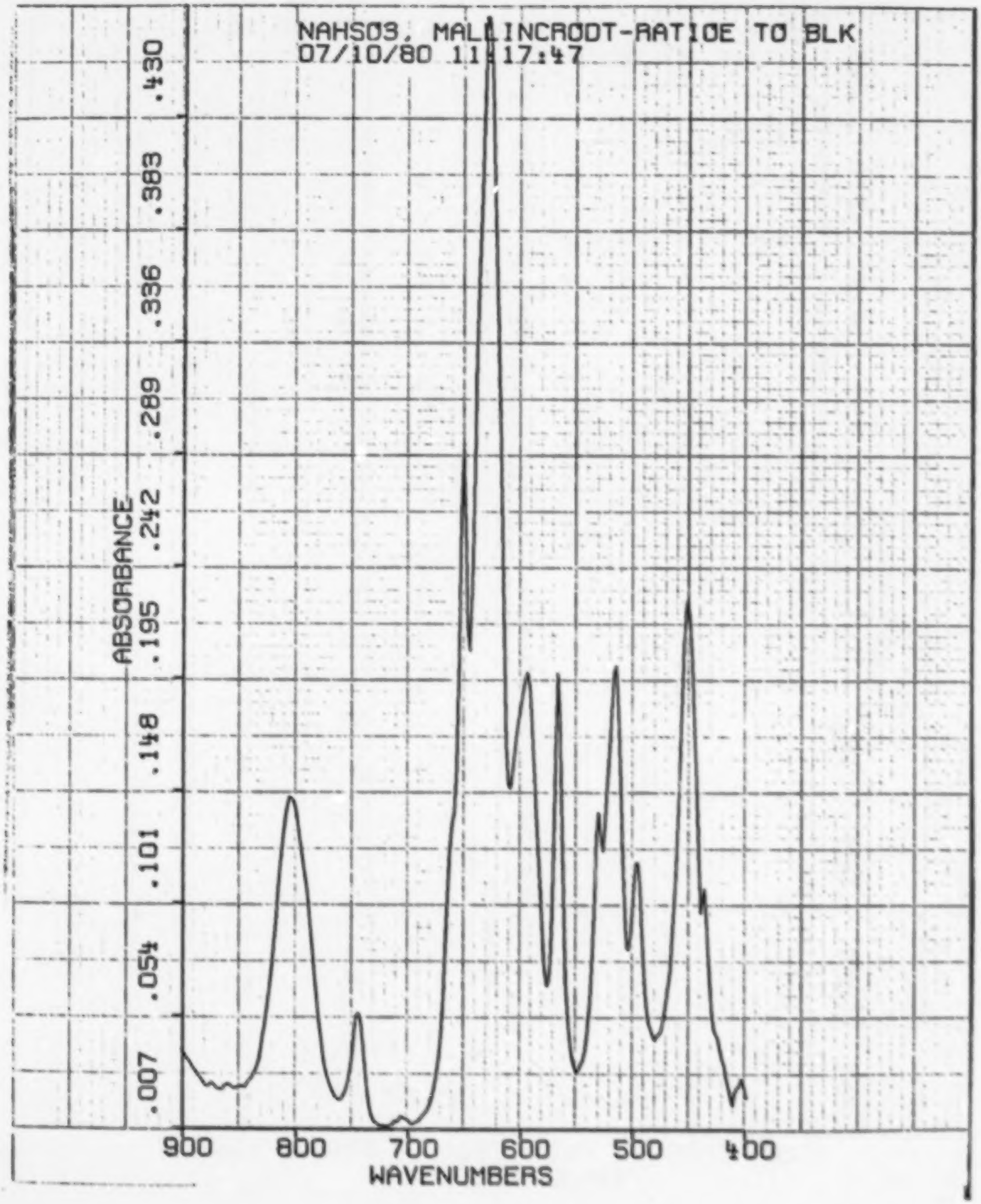


Figure D-4. Sodium Bisulfite Standard

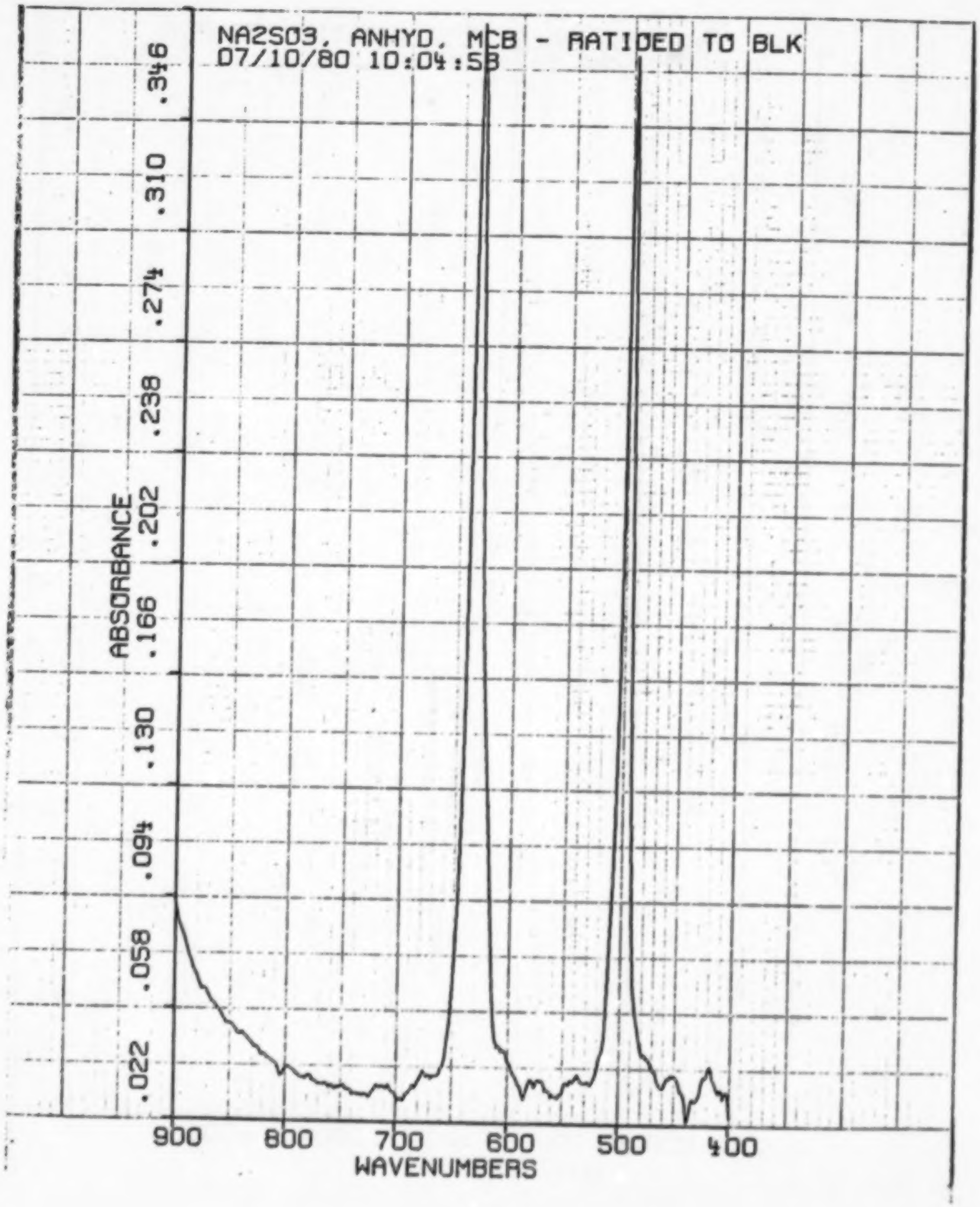
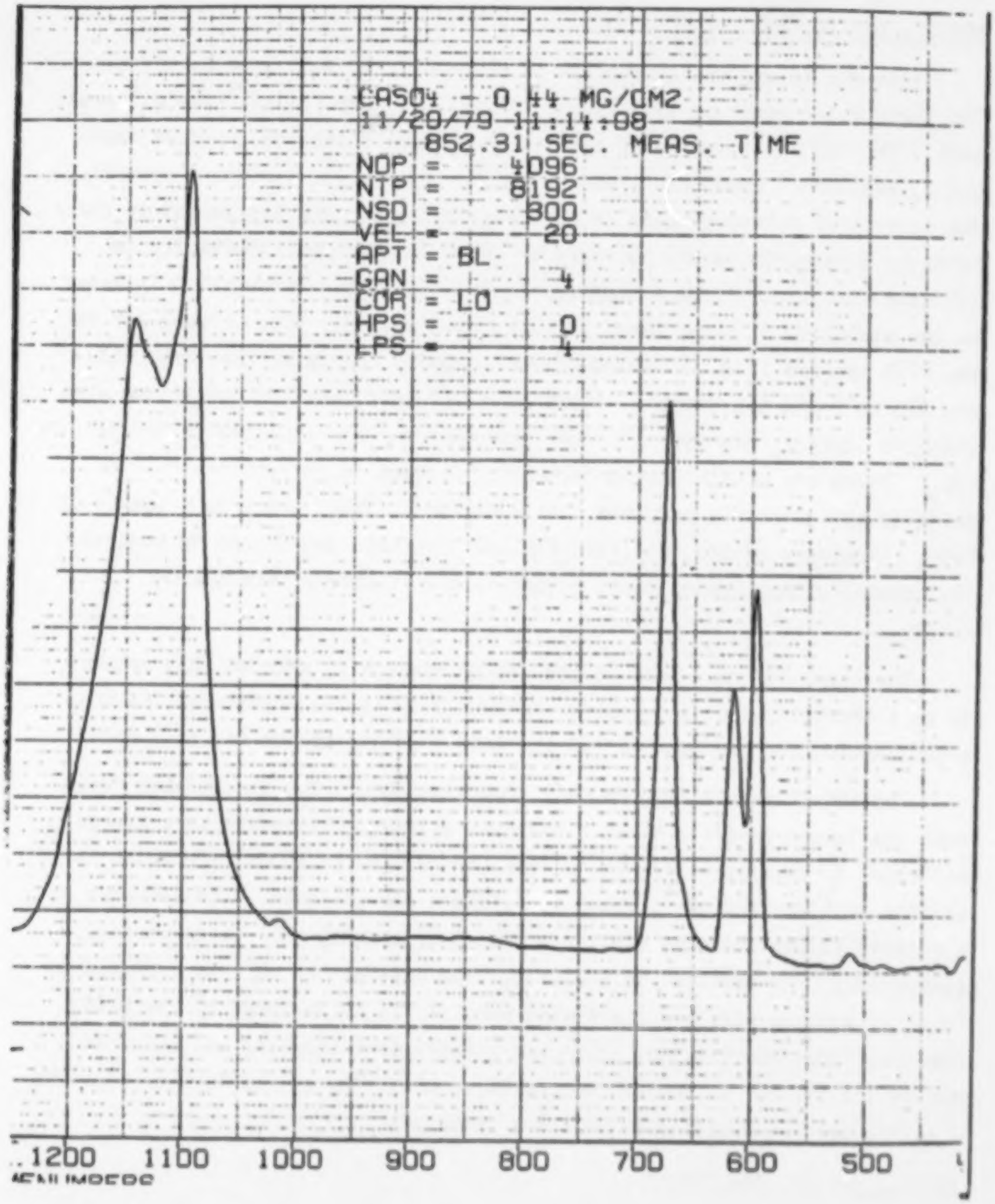


Figure D-5. Sodium Sulfite Standard



```
CASO4 - 0.44 MG/CM2
11/20/79 11:14:08
     852.31 SEC. MEAS. TIME
NOP  =     4096
NTP  =     8192
NSD  =      800
VEL  =       20
APT  = BL
GAN  =        4
COR  = LO
HPS  =        0
LPS  =        4
```

Figure D-6. Calcium Sulfate Standard

164-CC, 164-1C, AND 164-PF

Both the CC and the 1C samples (Figures D-7 and D-8) were fairly similar. The three major bands at 1075 (s,b), 795 (m), and 460 (s) cm^{-1} are all present. The 1050 cm^{-1} in the IC samples shows more splitting, perhaps indicating additional compounds present. These three major bands are probably due to mineral matter present in the original coal. The assignment of these bands as mineral in nature is based on their location and similarity to silicate minerals, and on a chemical test. The latter information is based on the stability of these bands to extraction with 1:1 HCl. Figure D-9 is the FTIR spectra of HCl extracted 164-CC sample. Bands at 795, 778, 693, and 460 cm^{-1} did not change. On the basis of this test and comparison with standard spectra, the 795, 778, 693, and 460 cm^{-1} are assigned to crystalline SiO_2. There are possibly other minerals included in the spectra, but no definite assignment is possible. In addition to SiO_2, there is evidence of $CaSO_4$ (shoulders at 595, 615, and 675 cm^{-1}) in both the CC and 1C samples. Its concentration appears to be higher in the 1C sample than the CC sample.

The sharp 440 cm^{-1} band in the 164-CC spectra is unknown but appears to be a thermally labile compound. Figure D-10 is the spectra of 164-CC after heating for one hour at 150 C. Note the loss of the 440 cm^{-1} band.

The 164-PF sample (Figure D-11) contains some SiO_2, though much less than the larger particle sizes. The band at 460, believed to be a mineral silicate, is shifted to 472 cm^{-1}. The strong band at 1000-1100 region is shifted to 1100-1200 cm^{-1}, which is evidence for sulfates. The presence of a sulfate is confirmed by the sharp 675, 615, and 595 cm^{-1} bands of $CaSO_4$ (anhydrous). In addition to the $CaSO_4$, the band at 562 cm^{-1} is assigned to Fe_3O_4 although a possible confirming band at 725 is obscured by the $CaSO_4$ spectra. Some confirmation of an extractable iron compound was obtained during the 1:1 HCl extraction of the CC sample. The extraction solution was a yellow color indicating Fe chloride compounds.

165-CC, 165-1C, AND 165-PF

The 165-CC (10 and 3 μm) sample (Figure D-12) was very similar to the 164-CC sample. Once again SiO_2 (crystalline) and silicate matrix was

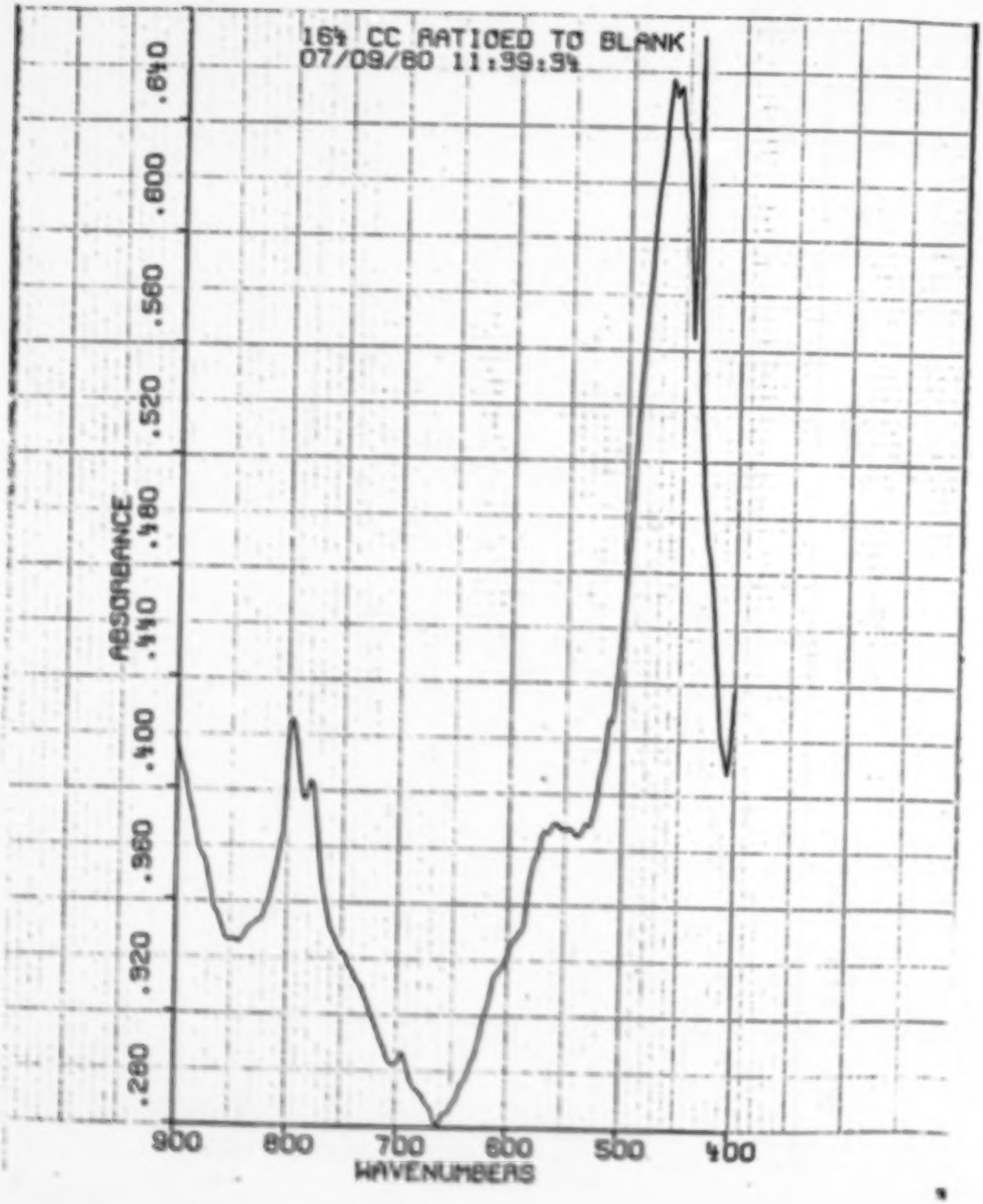


Figure D-7. Air Heater Inlet Particulate Larger Than 3 μm

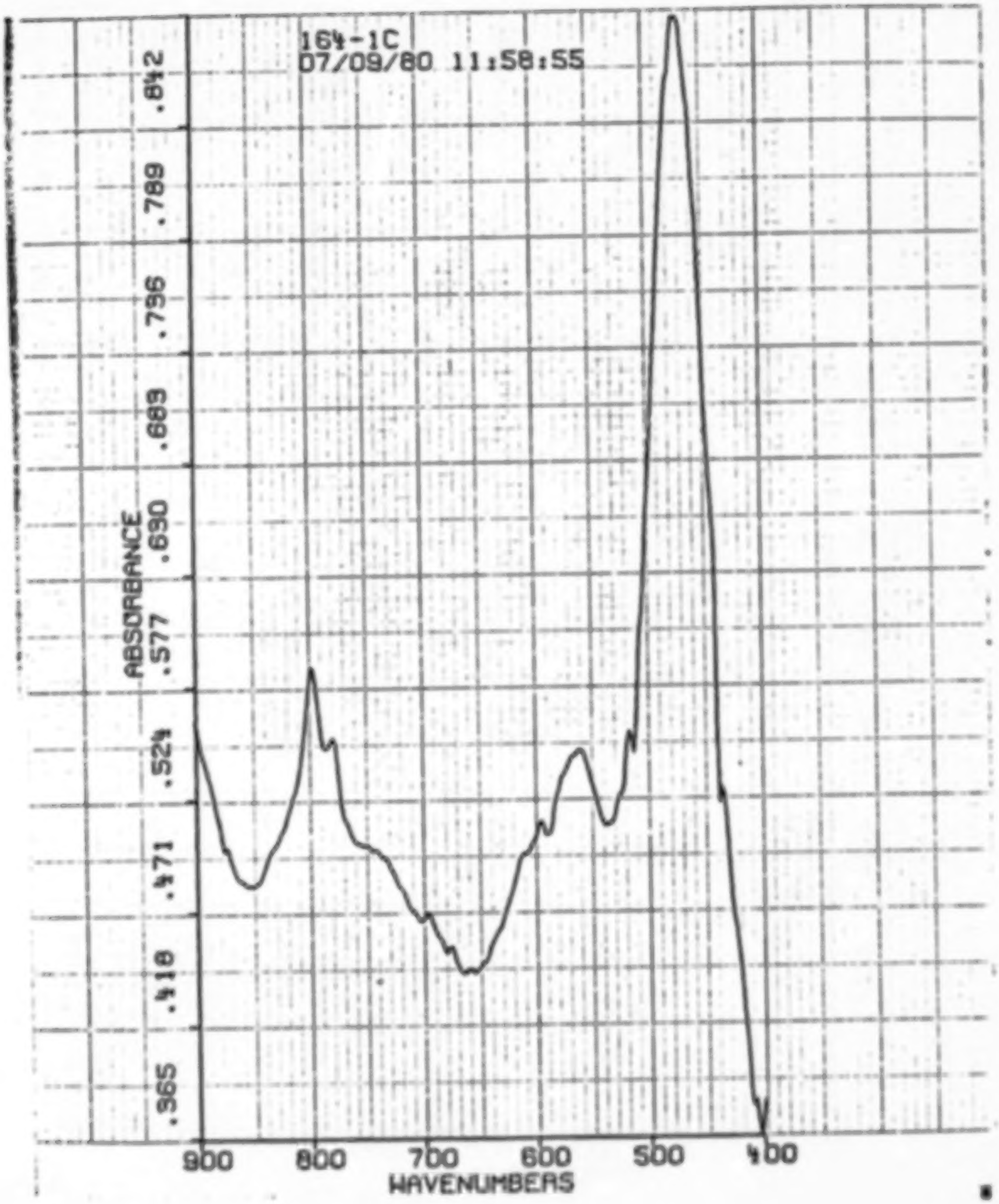


Figure D-8. Air Heater Inlet Particulate, 1-3 µm

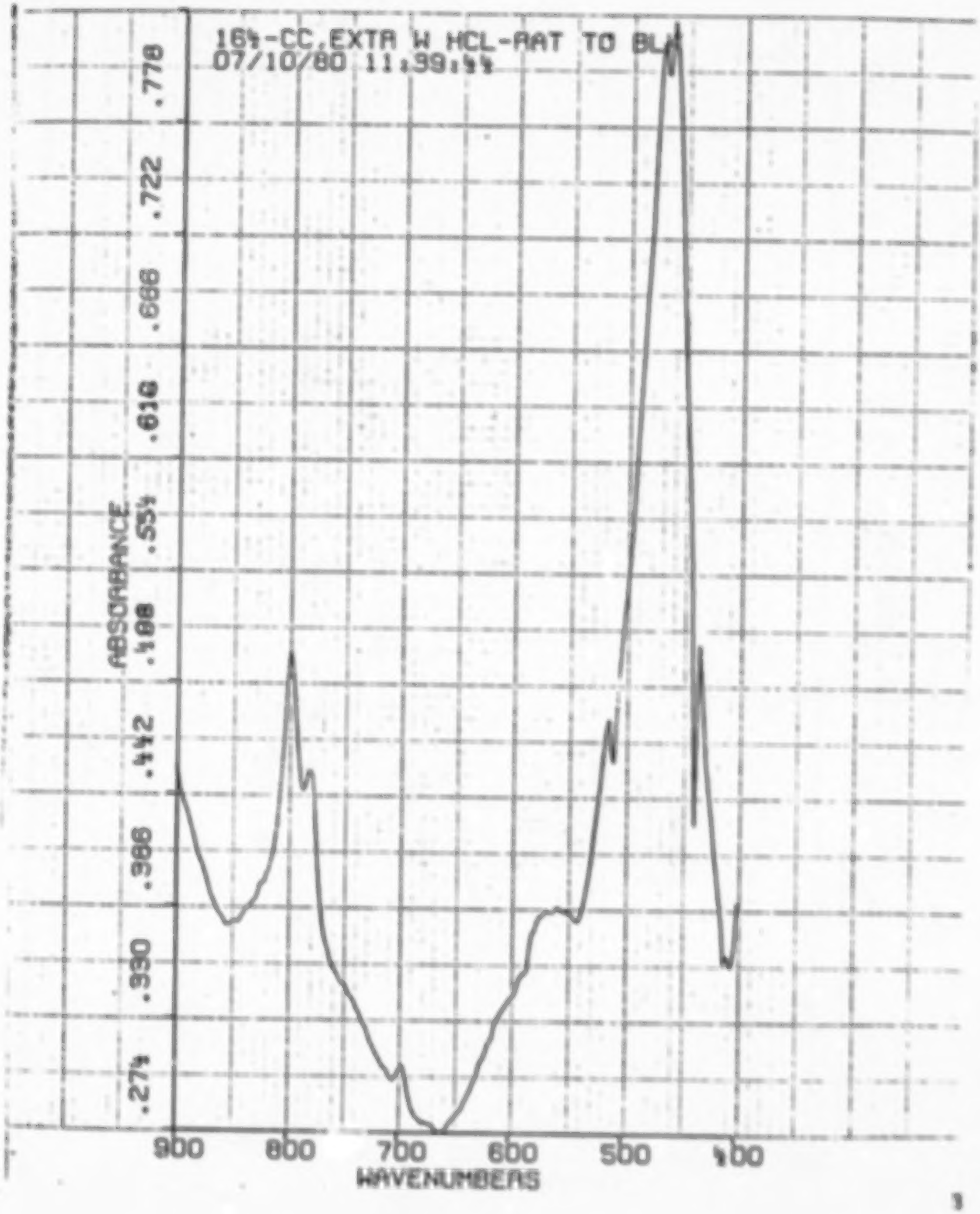


Figure D-9. HCl Extracted Air Heater Inlet Particulate Larger Than 3 μm

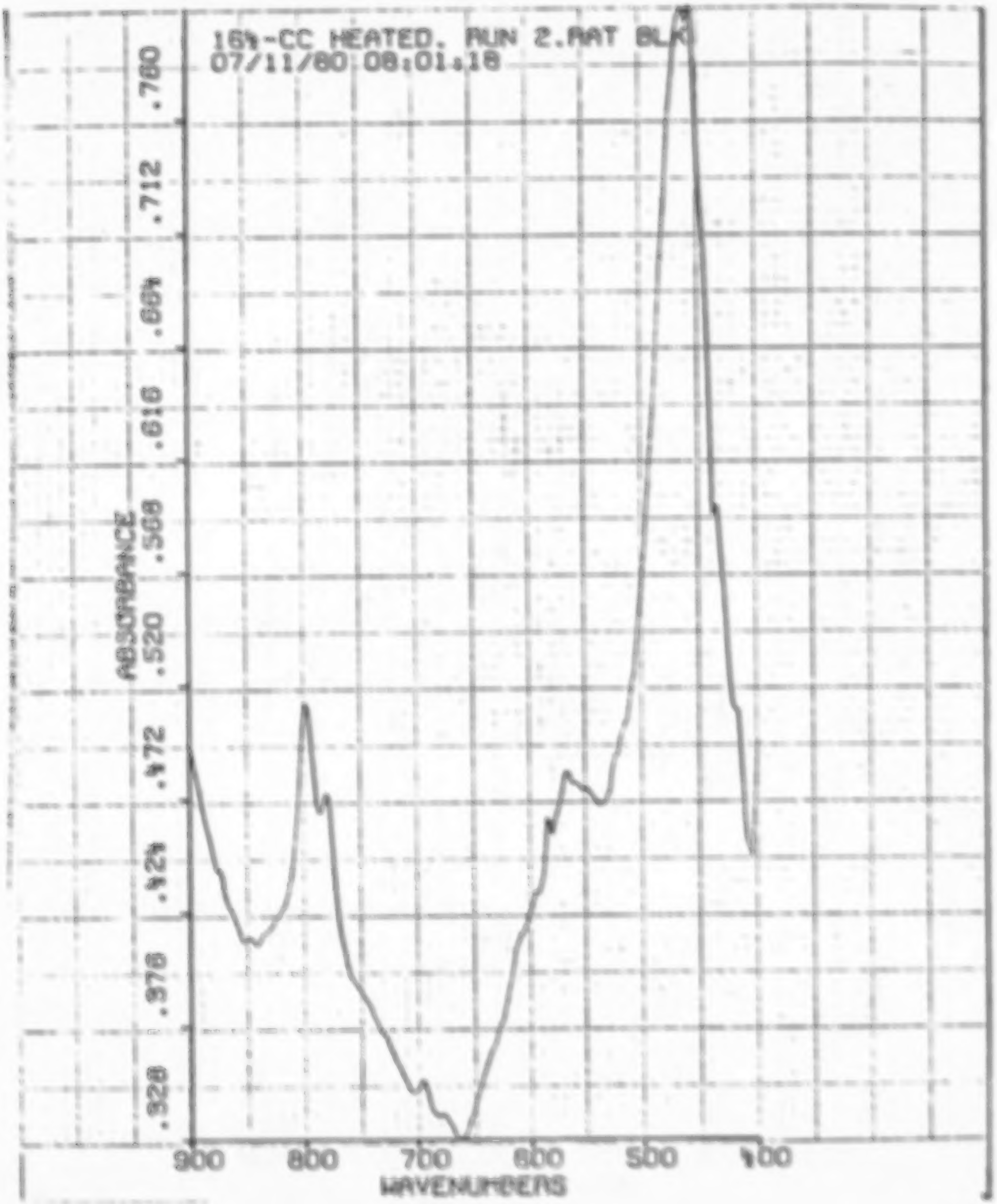


Figure D-10. Heat Treated Air Heater Inlet Particulate Larger Than 3 µm

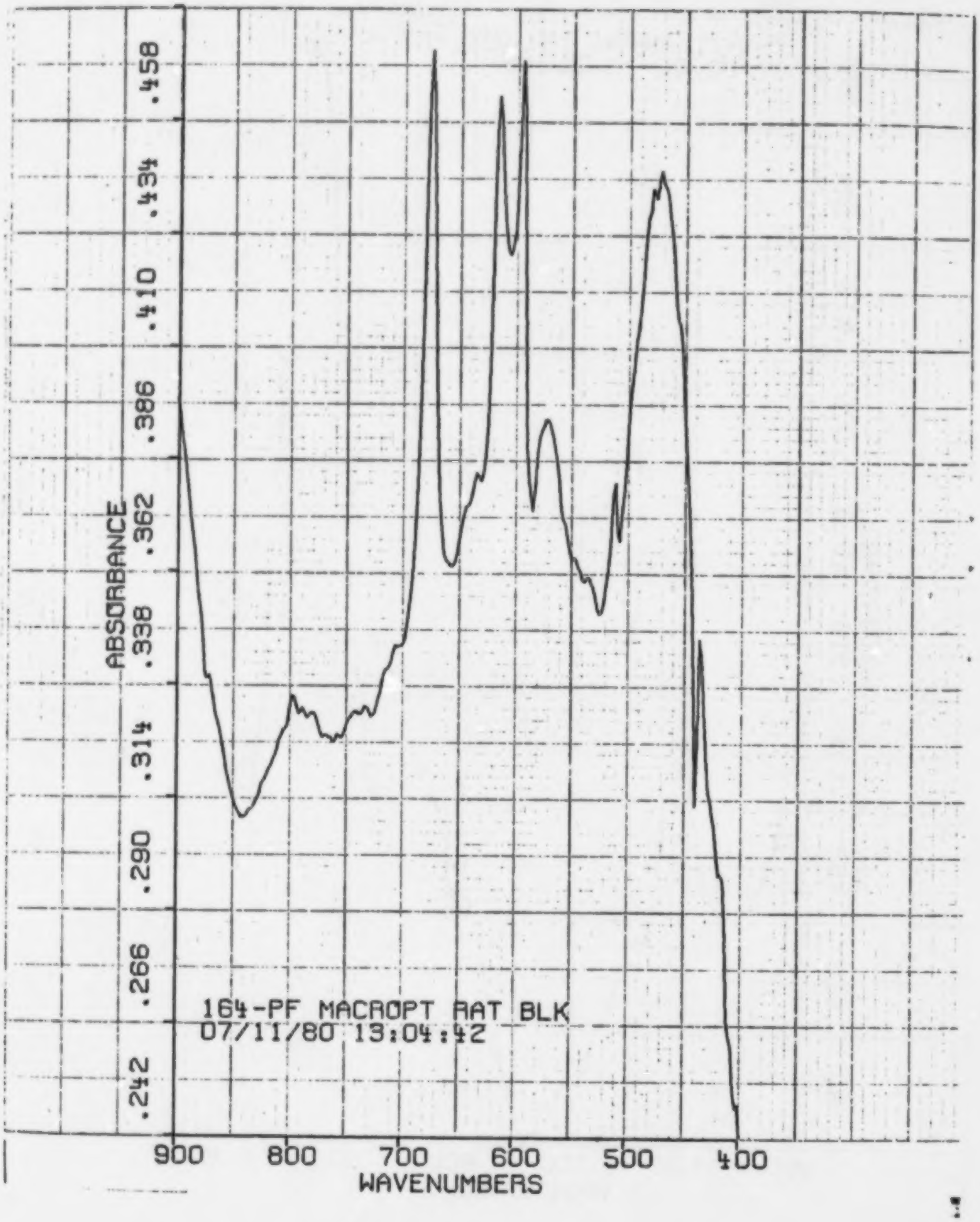


Figure D-11. Air Heater Inlet Particulate Smaller Than 1 μm

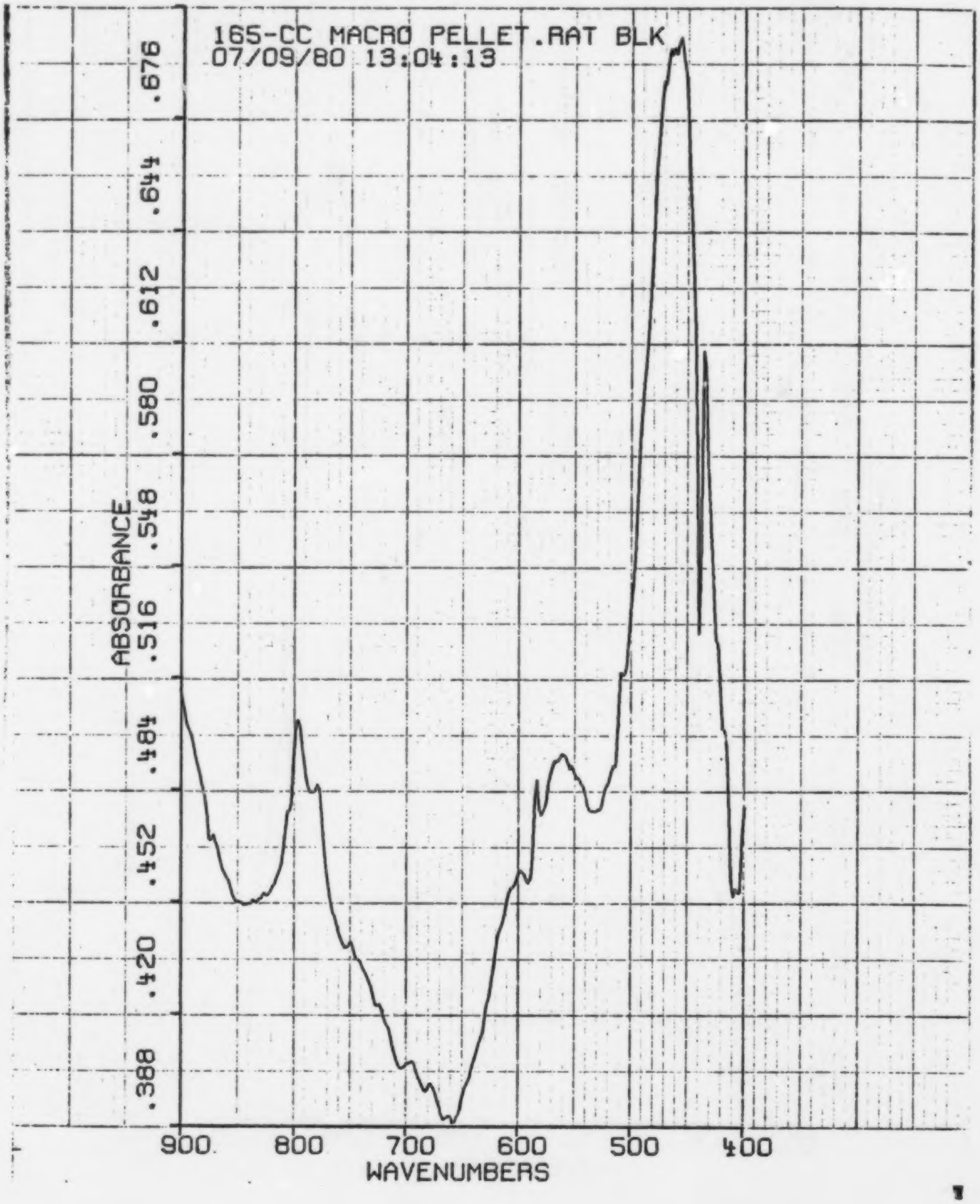


Figure D-12. Scrubber Inlet Particulate Larger Than 3 μm present. Evidence for $CaSO_4$ was definitely there, but since each band was present as a shoulder (600,620, 678 cm^{-1}), the amount of $CaSO_4$ must have been very low. Evidence for Fe_3O_4 (560 and 722 cm^{-1}) was found.

The 165-1C sample (Figure D-13) was different from the 164-1C. The SiO_2 content was much lower as evidenced by the decrease in the 795 and 778 cm^{-1} bands. The concentration of $CaSO_4$ was much stronger, while the band assigned to Fe_3O_4 is about the same intensity as the 164-IC sample. There is evidence of an additional sulfate present. Bands at 575, 605, 845, and 875 cm^{-1} could possibly be due to $NaHSO_4$ or $ZnSO_4$, though $ZnSO_4$ is a better match.

The particulate matter from the 165 filter (Figure D-14) is very different from 164-PF. Little SiO_2 is present, and the presence of Fe_3O_4 is questionable. From the width of the band at 1150, both sulfates (1100 → 1200) and silicates (1000 to 1100) are present. Calcium sulfate is indicated by the 1095, 1145, and 678 cm^{-1} bands. The key bands at 595 and 615 are obscured by strong band at 612 cm^{-1}. The 595 cm^{-1} $CaSO_4$ band is probably the shoulder of the 612 cm^{-1} band, but the 615 cm^{-1} $CaSO_4$ is completely obscured by an unknown band at 612 cm^{-1}. Based on the band position, a sulfate compound is indicated. Possible cation candidates are Fe, Al, Ca, Na, Mg, and Zn based on the elemental data. $FeSO_4 \cdot 7H_2O$ fit fairly well (615s, 730W), but the presence of Fe^{+2} under oxidizing conditions seems unlikely. None of the rest of the sulfate compounds of those elements match very well. It definitely is not $NaHSO_4$ since a strong band at 580 cm^{-1} would be expected. In addition to the unknown at 612 cm^{-1}, a band at 654 cm^{-1}, which may or may not be associated with the 612 cm^{-1} band, is also unknown.

166-PF

At the outlet of the wet scrubber only the SASS particulate filter collected sufficient material to enable compound identification analyses. The sample obtained, 166-PF (Figure D-15), was similar to 164-PF, but not at all like 165-PF. $CaSO_4$ is definitely present (595, 618, and 675 cm^{-1}), but Fe_3O_4 and SiO_2 seem to have disappeared. The evidence for a silicate matrix (475 cm^{-1}) is there and, in addition, bands for $NaHSO_4$ are definitely present (585, 620, 850, and 872 cm^{-1}). The 620 cm^{-1} $NaHSO_4$ band overlaps

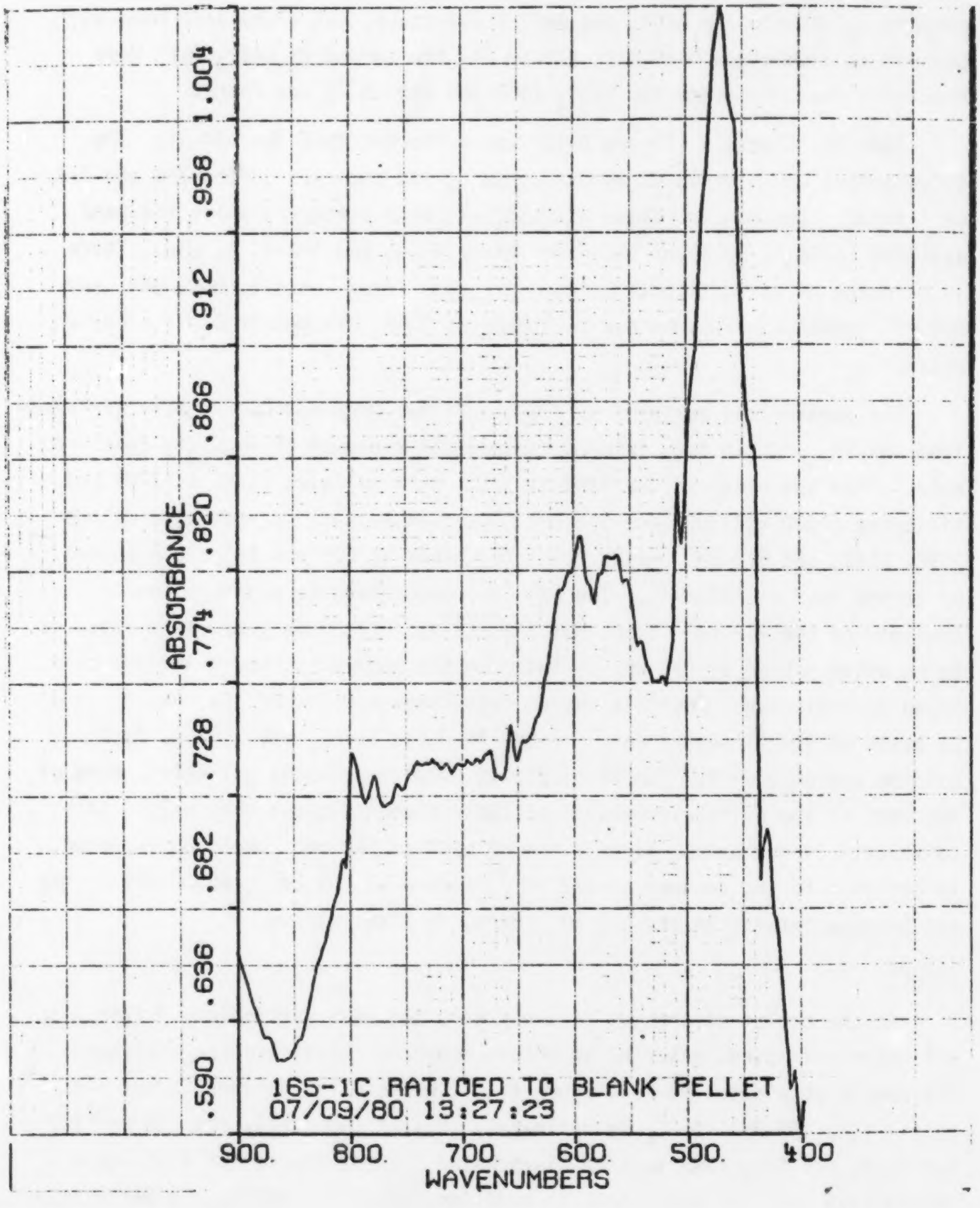


Figure D-13. Scrubber Inlet Particulate, 1-3 μm

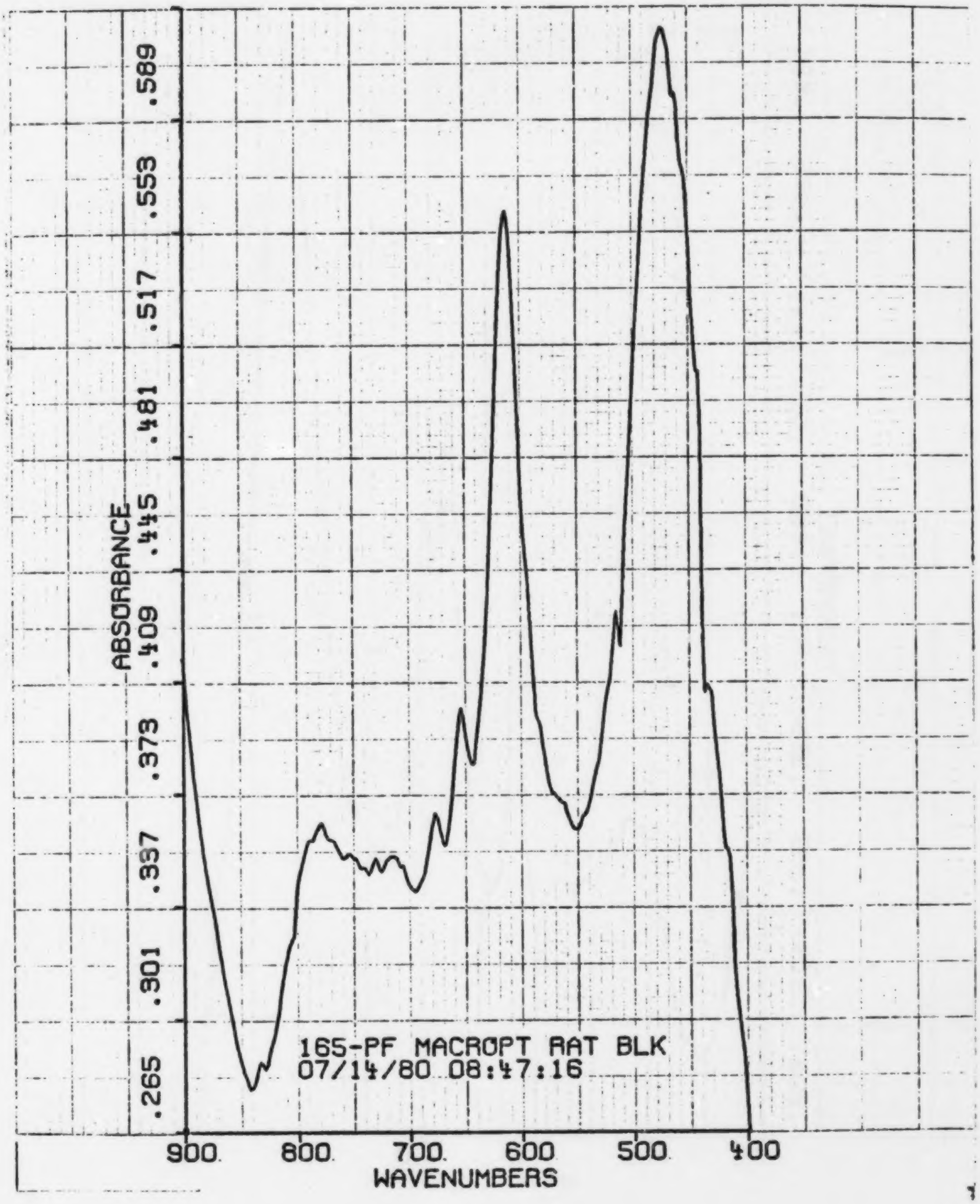


Figure D-14. Scrubber Inlet Particulate Smaller Than 1 μm

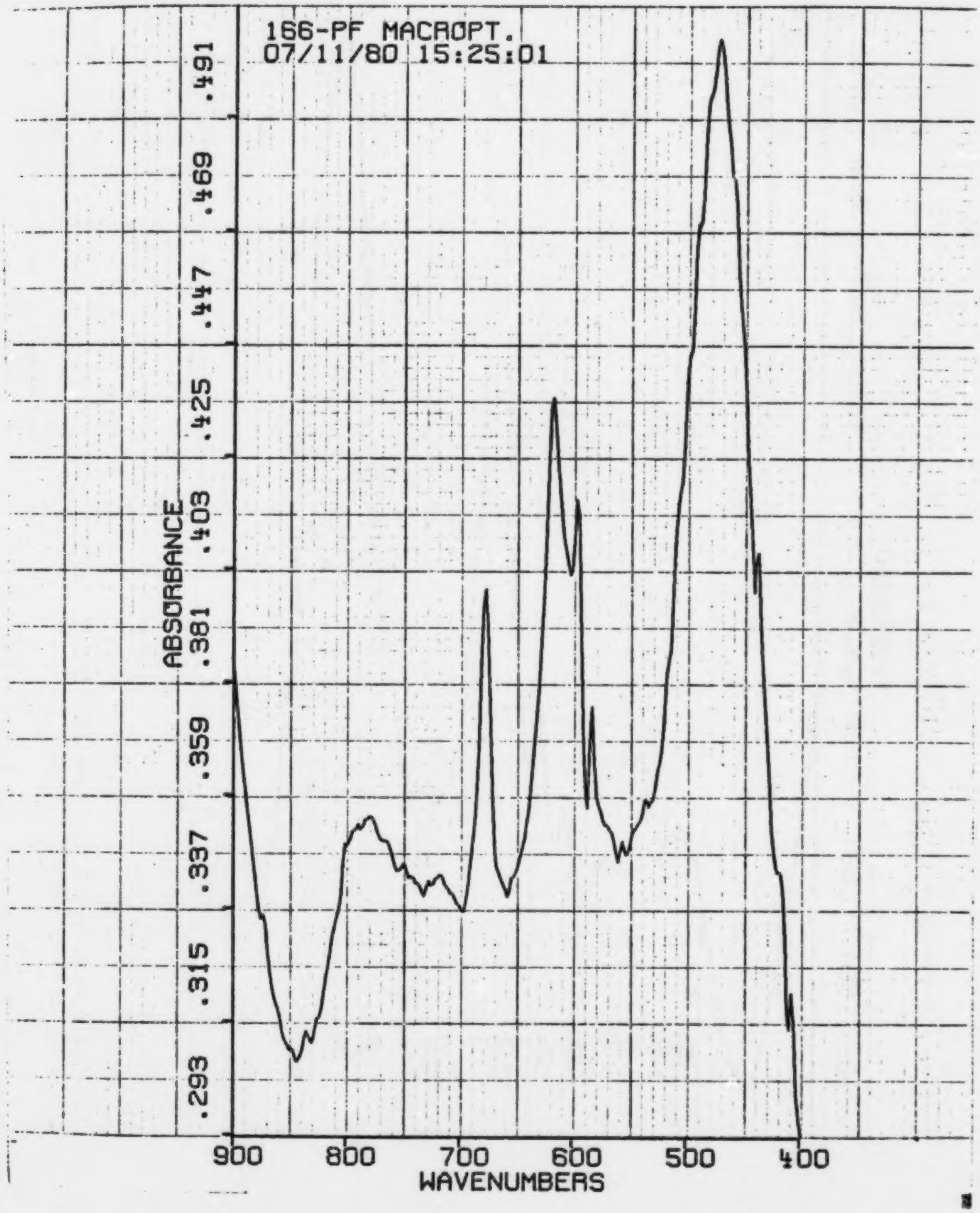


Figure D-15. Scrubber Outlet Particulate Smaller Than 1 μm with the 618 cm^{-1} of the $CaSO_4$ and is the reason why the height ratio between the $CaSO_4$ 595 and 618 cm^{-1} bands has been reversed in favor of the 618 cm^{-1} band.

The source of $NaHSO_4$ could be: 1) H_2SO_4 aerosols (formed after the H_2SO_4 vapor was cooled by the FGD) collecting on the filter and leaching Na^+ from the glass fiber, or 2) $NaHSO_3$ emissions from the FGD which are later oxidized to $NaHSO_4$ on the filter. If the H_2SO_4 aerosol collection was the primary source of $NaHSO_4$, than the $SO_4^{=}/Na^+$ ratio would be very high for 166-PF sample. Table D-2 summarizes the Ca, Na, and $SO_4^{=}$ analysis of 166-PF and 165-FC. Clearly $SO_4^{=}$ is in excess of the Na^+ concentration for 166-PF, but more than 50% of the $SO_4^{=}$ (mole basis) is accounted for by the Na^+ concentration assuming $NaHSO_4$ is the primary species found. If H_2SO_4 alone was producing $NaHSO_4$ by leaching Na^+ from the filter, the $SO_4^{=}/Na^+$ ratio would tend to be much higher; this is because Na^+ from the filter would have been cancelled when the filter blank was subtracted from the filter. It thus appears that the $NaHSO_4$ is from the emission of $NaHSO_3$ from the FGD. Additional evidence is derived from the chemical analysis of 165 FC (1 μm + filter sample). There the Ca^{+2}/Na^+ ratio is >1 compared to the 166-PF Ca^{+2}/Na^+ ratio which was <1, and the Ca^{+2} mmole concentration exceeded the $SO_4^{=}$ mmoles. These chemical data, the lack of evidence of $NaHSO_4$ in the 165-PF sample, and the disappearance of SiO_2 and Fe_2O_4 all indicate a change in the chemical composition of the particulate as a result of flue gas scrubbing.

SUMMARY

Table D-3 summarizes the compound information obtained from the FTIR study. A qualitative comparison of the chemical composition of different particle sizes at different locations is included. In addition to the results in Table D-3, the following conclusions were drawn:

1) SiO_2 was concentrated in the larger particle sizes.
2) $CaSO_4$ and Fe_2O_4 were mostly found in the <1 μm particle size.
3) The presence of $NaHSO_4$ in the outlet particulate matter is believed to be from the oxidation of $NaHSO_3$ emitted from the FGD.

TABLE D-2. CORRELATION OF Na, Ca AND $SO_4^{=}$ CONCENTRATION IN 166-PF AND 165-FC

Sample	Species	mg	mmoles
166-PF	Na^+	20.64	0.90
	Ca^{+2}	5.33	0.13
	SO_4^{-2}	162.63	1.69
165-FC	Na^+	14.77	0.64
	Ca^{+2}	81.91	2.04
	SO_4^{-2}	157.90	1.64

TABLE D-3. SUMMARY OF FTIR ANALYSIS OF NIPSCO FLUE GAS PARTICULATE MATTER

Sample	Sample Type and Location	Species Found	Certainty of Identification	Concentration Comparison Between Particle Sizes	Concentration Comparison Between Locations
164-CC	10 + 3 μm cyclone catch at the air heater inlet	SiO_2	Strong	Not Applicable	Not Applicable
		"Silicate matrix"	Strong		
		$CaSO_4$	Weak		
		Fe_3O_4	Very weak		
164-1C	1 μm cyclone catch at the air heater inlet	SiO_2	Strong	Less than 164-CC	Not Applicable
		"Silicate matrix"	Strong	Less than 164-CC	
		Fe_3O_4	Moderate	More than 164-CC	
		$CaSO_4$	Moderate	More than 164-CC	
164-PF	Filter catch at the air heater inlet	$CaSO_4$	Strong	Much more than 164-1C	Not Applicable
		Fe_3O_4	Moderate	Less than 164-1C	
		"Silicate matrix"	Strong	Less than 164-1C	
		SiO_2	Strong	Much less than 164-1C	
165-CC	10 and 3 μm cyclone catch at the scrubber inlet	SiO_2	Strong	Not Applicable	Same as 164-CC
		"Silicate matrix"	Strong		Same as 164-CC
		Fe_3O_4	Moderate		More than 164-CC
		$CaSO_4$	Moderate		Same as 164-CC
165-1C	1 μm cyclone catch at the scrubber inlet	SiO_2	Strong	Less than 165-CC	Less than 164-CC
		"Silicate matrix"	Strong	Less than 165-CC	Less than 164-CC
		Fe_3O_4	Moderate	Same as 165-CC	Less than 164-CC
		$CaSO_4$	Moderate	More than 165-CC	More than 164-CC
		$NaHSO_4$	Weak	Not Applicable	Not Applicable
		$ZnSO_4$	Very weak	Not Applicable	Not Applicable
165-PF	Filter catch at the scrubber inlet	"Silicate matrix"	Strong	Same as 165-1C	More than 164-PF
		$CaSO_4$	Weak	More than 165-1C	Much less than 164-PF
		$NaHSO_4$	Very weak	Same as 165-1C	Not Applicable
		(Unknown sulfate)	Not Applicable	Not Applicable	Not Applicable
166-PF	Filter catch at the scrubber outlet	$CaSO_4$	Strong	Not Applicable	More than 165-PF
		$NaHSO_4$	Strong		More than 165-PF
		"Silicate matrix"	Strong		Less than 165-PF

APPENDIX E

METRIC CONVERSION FACTORS AND PREFIXES

CONVERSION FACTORS

To convert from	to	Multiply by
Degrees Celsius (°C)	Degrees Fahrenheit (°F)	$t(^{\circ}F) = 1.8\, t(^{\circ}C) + 32$
Joule (J)	Btu	9.478×10^{-4}
Kilogram (kg)	Pound-mass (avoirdupois)	2.205
Kilojoule/kilogram (kJ/kg)	Btu/lb_m	4.299×10^{-1}
Megagram (Mg)	Ton (2000 lb_m)	1.102
Megawatt (MW)	Horsepower (HP)	1.341×10^{3}
Meter (m)	Foot (ft)	3.281
$Meter^3$ (m^3)	$Foot^3$ (ft^3)	3.531×10^{1}
$Meter^3$ (m^3)	Gallon (gal)	2.642×10^{2}
Nanogram/joule (ng/J)	lb_m/million Btu	2.326×10^{-3}
Picogram/joule (pg/J)	lb_m/million Btu	2.326×10^{-6}
Pascals (Pa)	Pound-force/$inch^2$ (psi)	9.450×10^{-4}

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
Peta	P	10^{15}	1 Pm = 1×10^{15} meters
Tera	T	10^{12}	1 Tm = 1×10^{12} meters
Giga	G	10^{9}	1 Gm = 1×10^{9} meters
Mega	M	10^{6}	1 Mm = 1×10^{6} meters
Kilo	k	10^{3}	1 km = 1×10^{3} meters
Milli	m	10^{-3}	1 mm = 1×10^{-3} meters
Micro	μ	10^{-6}	1 μm = 1×10^{-6} meters
Nano	n	10^{-9}	1 nm = 1×10^{-9} meters
Pico	p	10^{-12}	1 pm = 1×10^{-12} meters